Author: Claeyssens, Frederik
Title: Fundamental studies of pulsed laser ablation.

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Fundamental Studies of Pulsed Laser Ablation

Frederik Claeyssens

A dissertation submitted to the University of Bristol in accordance with the requirements of the degree of Doctor of Philosophy in the Department of Chemistry December 2001.

Approximate number of words: 70.667
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Abstract

The pulsed ultraviolet ($\lambda = 193, 248$ nm) laser ablation of graphite, polycrystalline diamond and ZnO targets has been investigated. Characteristics of the resulting plumes of ablated material have been deduced using optical emission spectroscopy (wavelength dispersed spectra, together with spatially and temporally resolved measurements) and electrostatic probes. Deposited films were analysed using a variety of techniques, including scanning electron microscopy, UV-visible absorption and Raman spectroscopy, and X-Ray diffraction.

The study of graphite ablation focused mainly on the identification and characterisation of laser-plume interactions. Such processes are very important in the creation of the highly excited ablation plasma. Laser-plume interactions were probed directly, by monitoring the absorption of the laser light by the ablation plasma, and indirectly, using optical emission spectroscopy (OES) and a Faraday Cup. Laser-plume interactions are shown to be responsible for the observed asymmetry (with respect to the surface normal) of the emission from C$^+$ species in the plume. Pulse duration effects were probed also, by comparing characteristics of the ablation process induced using short (~picosecond) and the more traditional (nanosecond) laser pulses. Raman spectroscopy on the deposited diamond-like-carbon films indicated that $sp^3$ fractions $>60\%$ are achievable.

Investigations on the ablation of ZnO targets (with and without added Al and Ga dopant) have resulted in a coherent view of the resulting plume, which exhibits a multi-component structure correlated with different regimes of ablation, which are attributed to ejection from ZnO and ablation from a Zn melt. OES measurements show that the emitting Zn component within the plume accelerates during expansion in vacuum – an observation attributable to the presence of hot, fast electrons in the plume. The same acceleration behaviour is observed in the case of Al atomic emissions resulting from ablation of an Al target in vacuum. Deposition conditions, substrate temperature and background gas pressure were all varied in a quest for optimally aligned, high quality ZnO thin films. Initial $ab\ initio$ calculations were performed also, to aid in understanding the stability of these $c$-axis aligned films.
Author's Declaration

I declare that the work in this dissertation is carried out in accordance with the Regulations of the University of Bristol. This work is original except where indicated by special reference in the text and no part of the dissertation has been submitted for any other degree. Any views expressed in the dissertation are those of the author and in no way represent those of the University of Bristol. The dissertation has not been presented to any other University for examination either in the United Kingdom or overseas.

[Signature]

Frederik Claeyssens
Dedications

For my mum, dad and sister
Acknowledgements

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For financial support I would like to thank the EPSRC.
We shall not cease from exploration
And the end of all our exploring
Will be to arrive where we started
And know the place for the first time

T.S. Eliot, "Four Quartets"
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1. General introduction to deposition of thin films and laser interaction with materials

This general introduction will discuss the relevance of laser ablation within the general field of thin film deposition. The field of thin film deposition is characterised by a myriad of different deposition techniques, all with their specific merits and disadvantages. Most of the techniques are developed for optimal deposition of one specific material. It is far beyond the scope of this chapter to discuss the details of these various techniques, and, since most of these techniques are a variant of a more general procedure, only a few general deposition techniques will be discussed.

The film deposition techniques will be discussed in the framework of the fundamental aspects of film growth, which will be described in some detail. The important fundamental parameters for film deposition will be addressed, and the different deposition techniques will be compared. The practicalities and the (possible) use in industry of each of the techniques will be discussed also.

In addition, a few examples of other applications of laser interaction with solid materials will be presented, namely the field of surface photochemistry, Matrix Assisted Laser Desorption and Ionisation (MALDI), the use of lasers in manufacturing of photonic components and in space technology. This list is of course not exclusive, since the whole field of laser interaction with materials is still developing, but gives a representative overview of a few of the trends in the field.

At the end of this chapter the scope of this thesis will be discussed and a general overview of the contents will be given.

1.1. Description of different deposition methods

1.1.1. Description of Pulsed Laser Deposition

The pulsed laser deposition (PLD) process is both conceptually and experimentally relatively simple. A laser beam is focused onto a target material placed in a high
vacuum chamber or a low pressure of background gas. The mere photon density on the target surface causes the ejection of neutral and ionised material via thermal and/or photochemical ejection mechanisms. The ejected material from a target arising after laser irradiation is called an ablation plume; it can consist of a plasma, a gas and a particulate component. The flux of material then impinges on a substrate, on which deposition takes place. The basics of the experimental technique are given in Figure 1.1.

Figure 1.1: Schematic of a basic PLD system.

1.1.2. Deposition Techniques

Different deposition techniques that are used in technology are given in Table 1.1, with the acronym used to describe the technique. As discussed the introduction of this chapter, this list is far from complete, but it gives an overview of the more important competing techniques for thin film deposition.
Technique | Acronym
--- | ---
Thermal Evaporation | TE
(Accelerated) Molecular Beam Epitaxy | (A)MBE
Cathodic Arc | CA
Laser Assisted/ | LA/
Metal Organic/ | MO/
Plasma Enhanced/ | PE/
Chemical Vapour Deposition | CVD
Sputtering (RF, Magnetron, ion beam) | S
Ion Beam Deposition | IBD
Pulsed Laser Deposition | PLD

Table 1.1: Different deposition techniques

TE is the easiest deposition technique, namely evaporative deposition of a target material either thermally, or by means of electron beam heating. MBE uses continuous molecular beams generated via Knudsen sources. If the beam is partially ionised by electron impact and accelerated towards the target via an electric field the process is defined as AMBE. CA uses a high current cathode/anode set-up to create a plasma from a conducting solid target, which is used as deposition flux. The deposition flux in CVD is derived from the reaction of two or more gases above a heated substrate; heating is generally necessary to sustain the reaction. Metals can be deposited by using metal-organic compounds as input gases (MOCVD) and the chemical reaction can be enhanced by sustaining a plasma above the substrate (PECVD) or by energy input via a laser beam (LACVD). Sputter deposition is performed by extracting ions (usually Ar\(^+\)) from a plasma at keV energies and arranging for them to strike a target consisting of the material to be deposited. The energetic Ar\(^+\) ions produce a continuous flux of sputtered atoms that deposit on a nearby substrate. IBD distinguishes itself from the other plasma deposition techniques because the plasma is generated remotely from the substrate; the ions are extracted by ion optics and accelerated towards the substrate.
1.1.3. Film Growth

Film growth and quality are dependent on a few fundamental parameters, namely the substrate temperature, the kinetic energy of the deposition flux and the deposition rate.\(^1\) Effects from background gas can also be included as a fundamental parameter. The importance of these parameters will be discussed, and the different techniques will be compared.

1.1.3.1. Substrate temperature

The temperature of the substrate is a highly important process parameter influencing the film morphology. In the initial stages of the film growth the flux deposited on the substrate might re-evaporate from the surface, nucleate into a cluster, be consumed by existing clusters or be trapped on a surface defect site. All these processes are dependent upon the mobility of the deposited atoms on the surface, and they each have their characteristic activation energies. Such surface rearrangements are possible at higher temperatures, while at low temperature they are inhibited.

Three modes of initial growth can be distinguished. These are shown in Figure 1.2.\(^2\) Island (Volmer-Weber) growth results in the formation of isolated islands on the surface. This occurs when the cohesive energy of the atoms within the film is greater than the cohesive energy between the film and atoms on the surface. Layer-by-Layer (Frank - van der Merwe) growth involves a deposition of one monolayer at the time and results in a very smooth epitaxial film. It occurs when the cohesive energy between the film and the surface atoms is greater than the cohesive energy of the film atoms. The cohesive energy will decrease monotonically as each film layer is added. Mixed growth involves growth of islands after the first monolayer has formed successfully. This occurs when the monotonic decrease in binding energy is energetically over-ridden by other factors such as strain due to lattice mismatch, with the result that island formation becomes more favourable.

The substrate temperature can have a profound influence on the film growth mechanism. For example, film growth via TE of metals has been modelled via Molecular Dynamics simulations at two different temperatures, 0 K and 0.4 \(T_m\) (where \(T_m\) is the melting temperature of the metallic film).\(^3,4\) Growth at 0 K is characterised as
Volmer-Weber growth, while film growth at higher temperatures follows the Frank – van der Merwe growth model.

![Figure 1.2: Different growth modes in thin film deposition, (a) Volmer-Weber growth, (b) Frank – van der Merwe growth and (c) mixed growth.]

The substrate temperature can also have a profound influence on the film thickening. The closer the temperature of the substrate to the melting temperature of the film, the more film relaxation channels are energetically accessible. At low temperatures (< 0.2 $T_m$), film growth proceeds via an athermal process, enabling metastable structures to grow. At higher temperatures (0.3 $T_m < T < 0.5 T_m$) grain boundaries within the film become mobile and surface diffusion and recrystallisation occurs. At the lower limit of this region the grain boundaries of just one preferred orientation may become mobile, giving preferential growth surfaces. At higher temperatures, surface and bulk diffusion and recrystallisation occur, yielding larger crystallites.

Clearly the microstructural morphology of the film is highly dependent on the growth temperature; indeed the temperature can be used as a process parameter to induce different structures. Metastable structures are grown preferentially at lower substrate temperatures, while the growth of crystalline materials will require higher (> 0.3 $T_m$) substrate temperatures to induce reconstruction and surface relaxation.

### 1.1.3.2. Energy of the deposition flux

Early film growth techniques employed deposition fluxes at thermal gas temperatures (> 0.1 eV). Growing films from species impinging at higher kinetic energies generally improves the film quality; this appears to have been first recognised by Mattox. The effects of high kinetic energy ion bombardment of the substrate
include ballistic collisions, ion mixing and thermally stimulated exchange mixing. These effects produce similar effects to raising the substrate temperature and govern film properties like film stress and crystal structure. An important manifestation of the similarity of the effects of temperature and incident kinetic energy is that high quality films can sometimes be deposited at lower substrate temperatures by using a high kinetic energy deposition flux.

The effects of a high kinetic energy deposition flux have been investigated via molecular dynamics simulations of Ag deposition on Ag at 300 K, as a function of incident particle kinetic energy. The calculation showed that the film grows in islands at low kinetic energies (< 10 eV) but that layer-by-layer growth dominates at higher kinetic energies. Ion mixing was also noticeable at higher kinetic energies (> 10 eV): some of the substrate atoms are located in the film and vice versa. This effect scales with impact energy and is associated with vibrational relaxation of the interface.

The above mechanism is still distinctly different from ion mixing during high-energy ion bombardment in which the ballistic collisions induce direct displacements of substrate atoms. The extent of displacements within the substrate is governed by the kinetic energy of the incident flux via the displacement energy. For example, the displacement energy for a bulk silicon atom is ~ 22 eV. Assuming that the surface displacement energy is half of this amount (11 eV) sets a window for the 'ideal' deposition conditions since, within this window, surface modification considered beneficial for film growth is allowed, while bulk displacement and ion mixing are minimised. Such purely ballistic collision effects are also dependent on the substrate atom mass, and the mass of the incoming atoms, since the energy transfer during collision is dependent on the mass difference between the species involved in the collision. A detailed study of the influence of the different parameters has been reported by Brice et al.

A second mechanism, in which high incident kinetic energies are important but where energy plays a contrary role to temperature, is during the growth of metastable films. The mechanism describing such film growth is the sub-plantation model, which finds extensive use in discussions of the growth of Diamond Like Carbon (DLC) films. Films with the highest sp³ fraction are characteristically grown in a deposition flux kinetic energy window of 100 to 200 eV. The DLC network grown under these conditions is compacted by these high-energy collisions. A deposition flux at lower energy induces to less compaction, while a deposition flux at higher energy gives rise to
sputtering. In contrast, increased temperature would be expected to induce thermodynamically favoured growth of the stable structure, i.e. graphite. Thus DLC films with high sp$^3$ content are grown preferentially at room temperature and with deposition flux kinetic energies of 100-200 eV. A consequence of this high kinetic energy is a large degree of ion mixing during deposition of these films: if grown on Si, a SiC interface exits between the film and the substrate.

1.1.3.3. Deposition Rate, vacuum quality and background gas

The rate at which material impinges on the surface (henceforth 'the deposition rate') is highly dependent on the material that is to be deposited and has to be considered on a case by case basis. Nevertheless, there are some general ground rules to consider. Too high a deposition rate will cause film deterioration because of the reduced opportunity for film relaxation. Too small a deposition rate, on the other hand, will result in unacceptably long deposition runs. The deposition rate is also correlated with the quality of the available vacuum since high deposition rates tend to put fewer demands on the vacuum quality. The lower the deposition rate, the more chance the film will incorporate unwanted gaseous impurities (common impurities include H$_2$O, CO$_2$, H$_2$ and N$_2$).

When depositing from multicomponent targets, the intentional introduction of background gas can enhance the film quality or can even enable the production of the multicomponent film (oxides or nitrides) from a monocomponent target and the appropriate reactive background gas (e.g. oxygen or nitrogen). Two additional effects can arise as a result of introducing background gas, namely, chemical reactions and / or non-reactive thermalising collisions between the energetic flux and the background gas.

Using high kinetic energy deposition fluxes in a background gas can induce gas phase reactions, which might aid in the deposition. Numerous examples can be given from the field of laser ablation, e.g. ablation of graphite in a nitrogen atmosphere under standard conditions gives rise to CN species, which are easily observed from their violet emission in the ablation plasma, and lead to production of C:N films with a nitrogen content that is related to the background pressure of nitrogen. A second example is the deposition via ablation of PbZrTiO$_3$. Pb atoms in the plume can be oxidised by a background pressure of oxygen. The ablated Pb atoms thus deposit as
PbO, which has a higher vapour pressure than Pb, and is retained more efficiently within the film.

Introduction of a background gas is not universally advantageous to all deposition techniques. As we have seen, the kinetic energy of highly energetic and directed fluxes can be usefully controlled by introduction of (reactive or non-reactive) background gas. On the other hand if the deposition flux does not have high kinetic energy and directionality it will be scattered by background gas collisions. In such cases the deposited film thickness drops precipitously as either the source-substrate distance or the pressure is increased.

1.1.4. Comparison of the different techniques for the different fundamental film growth parameters

Table 1.2 gives an overview of the requirements and performance of the different deposition techniques assessed against various different fundamental criteria.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Energy Range (eV)</th>
<th>Vacuum Requirement</th>
<th>Multi-Element Control</th>
<th>Background Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE</td>
<td>0.1</td>
<td>HV</td>
<td>Difficult</td>
<td>No</td>
</tr>
<tr>
<td>(A)MBE</td>
<td>0.1/0.1-100</td>
<td>UHV</td>
<td>Moderate</td>
<td>No</td>
</tr>
<tr>
<td>CA</td>
<td>0.1-1000</td>
<td>HV</td>
<td>Moderate</td>
<td>Yes</td>
</tr>
<tr>
<td>CVD</td>
<td>0.1/0.1-500</td>
<td>HV</td>
<td>Moderate</td>
<td>Yes</td>
</tr>
<tr>
<td>S</td>
<td>1-1000</td>
<td>HV</td>
<td>Easy</td>
<td>No</td>
</tr>
<tr>
<td>IBD</td>
<td>50-1000</td>
<td>UHV</td>
<td>Difficult</td>
<td>No</td>
</tr>
<tr>
<td>PLD</td>
<td>1-1000</td>
<td>HV</td>
<td>Easy</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 1.2: Different deposition criteria

The fundamental criterion of temperature control is omitted from the list since substrate temperature control can be easily included in the set-up for each technique. The kinetic energy range in most of the techniques is quite versatile, with the exception of TE, which only gives thermalised fluxes. (A)MBE and IBD require ultra high...
vacuum because of the small film deposition rate obtained in these techniques, which make them very sensitive to contaminants.

Multi-element control refers to the ease with which deposition rates can be accurately controlled when two or more species are deposited simultaneously. This criterion is most important for deposition of electronical components, because of their sensitivity to the precise stoichiometry. Only PLD and S can be described as 'easy' when it comes to producing a given stoichiometry, since these techniques use erosion of a target material to produce the deposition flux. In all other methods the deposition flux is produced from separate sources, each carrying one of the components of the film, which imposes much higher demands on the control system to produce a given film stoichiometry.

The introduction of background gas allows the opportunity to control further the stoichiometry. PLD has a significant advantage to other techniques since it shows high versatility with regard over this criterion ($P \leq 300$ mTorr), while other techniques generally only incorporate lower pressures of background gas. The techniques of TE, (A)MBE, S and IBD are not really compatible with any background pressure. Deposition rates are highest for CVD, TE and CA; PLD and (A)MBE and IBD have smaller deposition rates.

We also note that some of the deposition techniques can be used in conjunction with one another. IBD can be used together with any other pulsed technique to incorporate, for example, nitrogen or oxygen into the films. This combination is called Ion Beam Assisted Deposition (IBAD) and can open new production routes for multi-component films.

1.1.5. Practical deposition criteria

For a technique to be practically viable it has to conform to additional criteria. One straightforward criterion for practicality is to assess which techniques are commonly used in industry. CVD, S, TE and MBE are used extensively. CVD is the building block for deposition in the semiconductor industry, in combination with MBE, which is used for depositing high quality epitaxial films. S is used in the semiconductor industry for depositing metallic layers for electrical connections, it is also used to put protective
metallic coatings on plastics and glass. TE is used for the production of optical and protective coatings and of electronic materials.

PLD and CA are at this moment not commonly used in industry and are still mainly experimental techniques. Cathodic Arc is a quite recent technique (first reported in 1991) and is still in development; its main disadvantage is that only conducting materials can be used as the target. PLD has a much longer history but still has a few practical problems, which make the technique unattractive to industry.

The main practical limitations of PLD are its relatively low duty cycle, the incorporation of particulates in the deposited films (not unique to PLD) and problems associated with scale-up since the technique is ideally suited to depositing on small substrates. All of these various problems have been subjected to a substantial number of studies.\textsuperscript{13-18}

For example, two approaches have been identified for reducing the particulate density in the film, i.e. changing the target to substrate set-up and increasing the target temperature. The target to substrate set-up can be changed in two different ways showed in Figure 1.3.

![Figure 1.3: Different target to substrate set-ups: (a) off-axis set-up and (b) off axis set-up with magnetic field.](image)

The first strategy for reducing the particulate density in the film involves an off-axis set-up, which has proven to be successful for the deposition of Ag-Co films.\textsuperscript{17} A more involved arrangement incorporates a magnetic field (to deflect the plasma) in combination with an off axis set-up. This technique has been shown to be effective in the deposition of TiC.\textsuperscript{18} The off-axis set-up is effective if the angular spread of the laser...
produced atomic and molecular species (in the ablation plume) is bigger than the angular spread of the laser produced particulates. The set-up with the magnet is reliant on the fact that the laser produced plasma (which includes molecular and atomic ions and electrons) can be deflected by a magnetic field while the ablated particulates are assumed to be electrically neutral and are not deflected by magnetic fields. Both techniques succeed in reducing the particulate density in the film but also cause a drastic reduction in the overall deposition rate. A much simpler route to reducing particulates in the deposited films involves heating the target to temperatures near to the melting point. This technique has been shown to be effective during deposition from metallic targets \(^1^6\), and gallium and aluminium-gallium alloys. \(^1^5\) This technique can not, of course, be applied to deposition from target materials with very high melting temperatures (e.g. ceramics, graphite).

The possibility of large area deposition is very important if the technique is to be scaled up. Homogeneous deposition of YBCO on 3 inch diameter sapphire wafers has been reported \(^1^4\) using an off axis rotating target and substrate assembly. YBCO deposition on 34 mm x 1 m stainless steel foils has been demonstrated also, \(^1^3\) but this still remains the Achilles' heel of the technique. Scaling up and developing a continuous process based on PLD has proven to be a laborious task to date.

As one can derive from this section, PLD is a technique that may be too difficult to implement as an industrial process. Nevertheless it has also been shown that the technique offers an unmatched versatility for depositing materials. In the next sections we will discuss the range of materials that are accessible with this technique.

### 1.2. Production of thin films via laser ablation

The production of different thin films via PLD has been illustrated in numerous papers, and here we can see the strength of the technique. PLD proves to be an excellent experimental technique for investigating the fundamentals of film deposition and the properties of new materials.

Table 1.3 summarises a few of the materials that can be deposited via laser ablation. Again, this list is not exhaustive. PLD is a rapidly developing field and the number of materials deposited by the technique is increasing rapidly; it is impossible to
give a full review in this section. Rather, it might be viewed as a personal overview of the status of PLD growth of (possible) industrially important materials.

<table>
<thead>
<tr>
<th>Class</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td>YBCO, ZnO, TiO, In:SnO</td>
</tr>
<tr>
<td>Nitrides</td>
<td>AlN, GaN, BN, CN</td>
</tr>
<tr>
<td>Carbon based films</td>
<td>DLC, Diamond, Carbon nanotubes, TiC</td>
</tr>
<tr>
<td>Metals</td>
<td>Al, Cu, Fe</td>
</tr>
</tbody>
</table>

Table 1.3: Different materials deposited with PLD

Given the range of materials that it is possible to deposit with PLD it is beyond the scope of this overview to summarise specific deposition conditions for the different materials. The given list comprises superconducting materials (YBCO), wide band gap semiconductors (ZnO, TiO, Nitrides, Diamond), cold cathode field emitters (DLC, Diamond, carbon nanotubes), tribological materials (DLC, TiC) and metals. Given the simplicity of the process there are almost no restrictions on the target material to be used. PLD with liquid target materials has been illustrated and even PLD of solid nitrogen and methane has been probed experimentally.

The other huge advantage of the technique relative to the other deposition methods is that it allows the possibility of introducing reasonable high pressures of background gas into the vacuum chamber. Such is often found to be necessary when depositing multicomponent films with specific stochiometry. It also enables creation of new materials during deposition, e.g. growth of nitrides or oxides from PLD of the respective single elemental materials in a background pressure of either oxygen or nitrogen. Such techniques can be developed further by introducing a pulsed flow of background gas (pulsed nozzle) or by depositing together with an ion beam arrangement.

Another strength of the technique can be seen when we look at the deposition of carbon films. By changing the deposition conditions, DLC (high vacuum, RT), diamond (O₂ or H₂ background gas and 500 °C) and single wall nanotubes (He gas flow, Co catalyst and 1200 °C) can be produced. PLD enables production of thin films of metastable materials like DLC, next to their more stable allotropes.
The deposition of Cu-Co Giant Magneto Resisting (GMR) thin films \(^{35}\) and of thin films of SrBi\(_2\)(Ta,Nb)\(_2\)O\(_9\) used in the production of non-volatile Random Access Memory (RAM) \(^{36}\) provide further illustrations of the use of PLD for the production of new materials.

### 1.3. New fields in the laser interaction with solids

The field of pulsed laser deposition is of course only a small part of a much larger field of interest, which is the interaction of laser light with solid materials. The next paragraphs give a few examples of fields related to laser ablation, along with a short discussion of their fundamentals.

#### 1.3.1. Surface photochemistry

One important part of surface photochemistry is the photochemistry of adsorbate molecules on a solid surface. The subject of surface photochemistry with photons in the energy range of a few eV (comparable with the energy of a chemical bond) is subject to a large number of publications and has been reviewed by Polanyi et al.\(^{37}\) The process of surface photochemistry can be divided in four different photochemical processes namely photodissociation (PDIS), photoreaction (PRXN), photodesorption (PDES) and photoejection (PEJ) in the adsorbed state. A schematic of the four processes is given in Figure 1.4.
PDIS refers to photodissociation of an adsorbed molecule, this may occur either directly or indirectly. Direct absorption of a photon of sufficient energy results in a Franck-Condon transition from the ground state to an electronically excited repulsive or predissociative potential energy surface. If the energy state is repulsive, bond fission is instantaneous and the dissociation is favoured relative to other competing decay mechanisms like energy transfer to the substrate. Indirect photodissociation is a process whereby the substrate absorbs photons and causes fission of a bond in the adsorbate. The substrate can either absorb a photon by electronic excitation of defects, impurities or plasmons and then pass the energy via an electronic to electronic energy transfer to the adsorbate, or it can transfer an electron to an antibonding orbital of the adsorbate (called Charge Transfer/PDIS), thereby causing it to dissociate.

The PDIS process often results in the formation of photofragments whose translational energies are in excess of the energy required to surmount the activation barrier to chemical reaction in the adsorbed state. Under suitable conditions (i.e. where inter-adsorbate distances are small and the orientation favours the chemical reaction), either by high coverage or formation of islands, this can lead to reaction between a photofragment and a neighbouring adsorbate molecule. This process, initiated by
absorption of photons by the adsorbate and involving adsorbate molecules only is called PRXN.

Photodesorption is defined as the process resulting in desorption of intact adsorbate molecules following absorption of photons by the substrate, whereas photoejection is reserved for the process resulting in desorption of intact molecules following photon absorption by the adsorbate. In the latter process the energy involved in the electronic excitation is converted into nuclear motion. Effects of the four different mechanisms are observed in adsorbates on metals, semiconductors and insulators as discussed in some length in reference 37.

1.3.2. Matrix Assisted Laser Desorption and Ionisation

Matrix Assisted Laser Desorption and Ionisation (MALDI) is an important and growing field. The technique involves irradiation of a laser absorbing matrix containing a small percentage of large molecules, e.g. biological molecules and polymers, which are transferred to the gas phase by desorption. This process is normally coupled to a mass spectrometer, which is used to measure the mass of the large molecules of interest. The technique is, to date, one of the most precise methods available for measuring the mass of biomolecules and polymers.

The fundamental theory of the technique is reviewed in the excellent papers of Garrison et al., 39-41 which describe theoretical modelling of MALDI via Molecular Dynamics (MD) simulations. Former MD simulations 42 treated all of the atoms in the molecules, making the process very demanding computationally, since the upper limit of the time steps in the MD simulation were determined by the timescales of intramolecular vibrations. Only short time runs (45 ps) were thus affordable. The studies give information on a microscopic level only and cannot be readily extrapolated to larger systems.

The model discussed in the papers of Garrison et al. 39-41 do not take the individual atoms into account but assume that molecules can be treated as spheres. These spheres either expand or break down into smaller spheres when they absorb a laser photon reflecting, respectively, the laser induced vibrational excitation or breakdown of the molecule. Treating the molecules as spheres enables calculation of the dynamics of much larger systems over much larger time-scales compared to the former MD studies.
This 'breathing spheres' model has been extremely successful in qualifying the MALDI process. It predicts the sudden change in evaporation yield with increasing fluence that correlates with the onset of ablation (compared to surface evaporation) as observed in experiment 43 (see Figure 1.5). It also predicts a highly forward peaked ablation plume, which cools down rapidly, explaining why MALDI is successful in evaporation of large molecules without fragmenting them in the process.

Figure 1.5: (a) and (b) are both snap shots of MD calculations for the same laser fluence and initial conditions, at the onset of the ablation regime. (a) Shows an evaporation regime where most of the ejected clusters are smaller than 4 molecules and (b) shows ablation behaviour where most of the clusters are bigger than 4 molecules. These figures illustrate the sharp transition between surface evaporation and ablation in MALDI.
1.3.3. Microshaping of Photonic Components

Microshaping of photonic components will be very important in the further development of the emerging field of photonics. One of the most important materials in photonics is fused silica, since it has a low absorption coefficient and is transparent over a broad wavelength range. Shaping of elements can be achieved via micromachining and etching but also by laser irradiation. Laser irradiation of this wide bandgap material (9.3 eV) has some intrinsic problems, not least because of its low absorption cross section, but also associated with poor process control.

The recent development of bench-top F2 excimer lasers ($\lambda = 157$ nm) offers a possibility of much improved process control. Holes drilled in fused silica with an F2 laser are incomparably smoother than those achieved using an ArF ($\lambda = 193$ nm) laser; indeed their quality is high enough to be used in photonic applications.

1.3.4. Laser Ablation in space technology

Laser ablation offers potential important developments in space technology which probably started off as a tangent to the infamous ‘Star Wars’ project of President Ronald Reagan. Two different possible applications of high power lasers in space technology are given by Phipps et al. One is to clear near Earth space of debris, the other example involves use of laser ablation to launch satellites into low Earth orbit.

Anthropogenic near Earth space debris is an issue that is becoming a serious threat to the security of long term space missions. Almost a million pieces of debris have been generated during the 35 years of space flight. The most economical solution to this problem is to cause the debris to re-enter Earth’s atmosphere to burn up. Due to the number, speed and spatial distribution of the debris, an agile source of mechanical impulse is required. A combination of a high-resolution optical detection mechanism and a ground based laser system might provide the impulse to de-orbit the objects. Figures provided suggest that a 20 kW, 530 nm laser could clear the near Earth space of debris larger than 1 cm but less massive than 100 kg within 4 years.

Launching small objects into low Earth orbit is also considered to be a feasible application of laser ablation. The object accelerates via ablation of solid material of the
satellite induced by a ground-based laser. This set-up can make the weight of the vessels much smaller since the need for a propelling rocket is removed, thus reducing the energy input required for putting small satellites into orbit. This is estimated to reduce the cost of launching 100-fold.

1.4. Scope of this thesis

This thesis concentrates on characterisation of the pulsed laser ablation processes of two materials, namely graphite and zinc oxide, and the study of the pulsed laser deposition of DLC (from graphite) and zinc oxide films.

Our study focuses on the detection and characterisation of the ablation plume via measurements of the optical emission and the charged components in the plume, thus providing a data set against which to test models for the ablation process. Such understanding of the processes governing laser ablation is fundamental to subsequent studies of the influence of the ablation / deposition process parameters on the properties of the grown films.

Graphite (DLC) and zinc oxide have been selected for their attractive properties, not only from an ablation viewpoint but also from a materials science point of view. DLC is currently used in the electronics industry as a wear resistant coating for hard disks. It is also a potential material for use as a cold-cathode field emitter. Zinc oxide thin films have a wide range of potential applications in the electronics industry. It is a wide band-gap semiconductor that can be doped easily with aluminium and gallium to produce transparent conductive films. The applications of lubricious zinc oxide coatings have also been investigated.

The ablation characteristics of the two different materials are also interesting from a fundamental point of view. The ablation of graphite is studied as an example of ablation of monocomponent materials. Its structural simplicity allows study of fundamental issues of laser ablation without 'blurring' from more complex phenomena related to multicomponent ablation. After this, the more complex ablation behaviour of zinc oxide has been studied. Fundamental issues relating to the ablation of two-component materials are addressed and explained.
The pulsed laser ablation and deposition of graphite has also been studied at a single wavelength (248 nm) with different laser pulse durations, namely 450 femtoseconds, 5 picoseconds and 35 nanoseconds. Laser excitation of the solid with these three different time scales (and thus intensities) reveals different ablation mechanisms and properties, which are reflected in the properties of the deposited films.

1.5. Conclusion

Laser ablation is, to date, one of the most versatile thin film deposition techniques with which to probe experimentally the production and properties of thin films. This experimental versatility runs counter to the usage of the technique in industry. Two practical deposition problems account for this lack of industrial usage. Laser ablation tends to produce not just a thin film, but also larger particulates which become incorporated in the film. This problem has been reported universally in deposition studies of all materials investigated. Scaling up of the technique is also proving difficult and, to date, most of the reported studies only involve use of small substrates (less than 1 inch diameter).

Research in laser ablation is at this moment focused on two areas, namely studies on the laser ablation process itself and of the film properties. Correlation of the two areas provides an integrated picture of the best process parameters to use when seeking to deposit a thin film with given properties. Next to this, although the general processes governing ablation are well understood, studies of the fundamentals of ablation of specific materials provide a more detailed and quantitative picture to strengthen the general theory, which will be discussed in Chapter 3.

This thesis emphasises this two-fold approach by seeking both qualitative and quantitative understanding of the laser ablation process of specific materials, correlating such results with the influence of the ablation conditions on the subsequent film deposition, and thereby providing a more profound understanding of the ablation process of the two materials, graphite and zinc oxide, discussed in this thesis.
1.6. References

Chapter 1: General Introduction

(2000)

Chapter 1: General Introduction

44 P. R. Herman, J. Yang, K. Kurosawa and T. Yamanishi. SPIE Proceedings, 2991, 170 (1997)
This chapter will discuss in detail the experimental set-up used for the pulsed laser ablation (PLA) and the pulsed laser deposition experiments. The experimental methods used include both plasma analysis techniques and thin film analysis techniques since the main focus of this thesis is to connect the characteristics of the laser ablated species with the properties of the as deposited films.

This chapter divides into three parts, namely the set-up of the laser and vacuum systems, the experimental techniques used to characterise the plume arising during pulsed laser ablation and the experimental techniques used to characterise the deposited films.

### 2.1. Lasers

The energy source for material evaporation and atomisation in a pulsed laser ablation experiment is a laser. The most favourable wavelengths for these type of experiments are short (UV) wavelengths such as those provided by excimer lasers, for reasons explained in Chapter 3. The popularity of these systems compared with the alternative Nd:YAG lasers stems from their high power output of UV photons without the necessity of frequency doubling (or quadrupling).

The artificial word excimer is an acronym for 'Excited Dimer' and characterises a class of molecules that fulfil the conditions for generation of a population inversion: a thermally unstable ground state (well depth of the order of $k_B T$) and excited states with a short radiative decay time (see Figure 2.1). The term excimer actually only correctly applies to homonuclear dimers. The correct term for heteronuclear molecules is excipllex (excited molecular complex), although excimer is commonly used also for the class of excipllex molecules.
Figure 2.1: Excimer laser operation, specified for an exciplex molecule, where H stands for the halogen atom and N for an inert gas atom and * depicts the excited state.

A transition from the upper electronic state to the electronic ground state results in a fast dissociation ($10^{-13}$ s) of these molecules into their constituent atoms. For this reason the ground state remains effectively unpopulated; any excited state population will thus constitute a population inversion, which can be used for lasing action. The wavelength of the lasing is determined by the vertical separation of the electronic states; different excimers yield different laser wavelengths. Most excimer lasers are based on inert gas halides such as ArF, although homonuclear excimers, such as F$_2$, also exist. An overview of the commonly used excimer systems is given in Table 2.1, along with their associated lasing wavelength.

<table>
<thead>
<tr>
<th>Excimer Laser</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$</td>
<td>157</td>
</tr>
<tr>
<td>ArF</td>
<td>193</td>
</tr>
<tr>
<td>KrCl</td>
<td>222</td>
</tr>
<tr>
<td>KrF</td>
<td>248</td>
</tr>
<tr>
<td>XeCl</td>
<td>308</td>
</tr>
<tr>
<td>XeF</td>
<td>351</td>
</tr>
</tbody>
</table>

Table 2.1: Different excimer lasing systems, each with their characteristic lasing wavelength.
Chapter 2: Experimental Techniques

The processes resulting in lasing are given in equations (2.1) to (2.5), where the * depicts an excited state of the molecule and M is the mediating body (or third body in three body reactions). The reactions are given for the ArF excimer laser, the reactions for the KrF excimer laser are similar and the inert gas atom Ar can be substituted by Kr.

\[
\begin{align*}
\text{Ar} + e^- & \rightarrow \text{Ar}^* + e^- \quad \text{(Electron impact excitation)} \quad (2.1) \\
\text{Ar} + e^- & \rightarrow \text{Ar}^+ + 2e^- \quad \text{(Penning ionisation)} \quad (2.2) \\
F_2 + e^- & \rightarrow F + F^- \quad \text{(Dissociative recombination)} \quad (2.3) \\
\text{Ar}^+ + F^- + M & \rightarrow \text{ArF}^* + M \quad \text{(Recombination stabilised by a third body)} \quad (2.4) \\
\text{Ar}^* + F_2 & \rightarrow \text{ArF}^* + F \quad \text{(Reaction)} \quad (2.5)
\end{align*}
\]

After lasing, the reaction products can reform the original reactants via reactions (2.6) and (2.7):

\[
\begin{align*}
\text{ArF}^* & \rightarrow \text{Ar} + F + h\nu \quad (2.6) \\
F + F + M & \rightarrow F_2 + M \quad (2.7)
\end{align*}
\]

In theory this regeneration scheme suggests that the laser gas mixture should last for ever but, in practise, the laser has to be refilled periodically because the highly reactive F₂ degrades through reaction with the laser cavity walls and because of laser cavity leaks. Given the importance of third body reactions, the laser is operated at high pressures (3 atmosphere) and the gas mixture is 0.16% F₂, and 6.3% Ar with the balance Ne.

The pulse duration of excimer lasers depends on the pumping mechanism. Pulse durations of tens of nanoseconds are obtained when using electrical discharge excitation. Shorter pulse durations (60 fs – 5 ps) require pumping of an excimer amplifier with the output of a short pulse dye laser. The experimental set-ups for both pumping methods are given in Figure 2.2.
In the nanosecond case, high pump powers (in the order of MW/cm²) and pulse durations in the order of tens of nanoseconds can be achieved via fast high-voltage switches (Thyratrons). The short time-scale of the discharge and, more importantly, the typical design of the cavity (shown in Figure 2.2(a)) allows only a single pass of the laser radiation through the cavity, in contrast with the multi-pass cavities used for Nd:YAG lasers. This results in a low degree of mode selection and consequently in low spatial and temporal coherence of the emitted light. The resulting laser beam is highly divergent (1 × 3 mrad), the line width is typical 1 nm, and the pulse duration is 10-50
ns. On the positive side, high laser pulse energies (typically 0.1 - 1 J) in the UV spectral range are easily obtainable with excimer lasers.

To obtain an excimer laser pulse of shorter duration a more complicated arrangement involving optical pumping of an excimer amplifier with a short pulse dye laser (shown in Figure 2.2(b)) is required. The EMG 150 Lambda Physik excimer laser is used as a pump laser (at 308 nm) for a special sub-picosecond dye laser amplifier system, and as an amplifier (at 248 nm) for the frequency-doubled output pulses of the dye laser set-up. Part of the output of the XeCl laser is used to pump a Distributed Feedback Dye Laser (DFDL), which in turn generates the pumping laser beam for the KrF laser cavity. This pump source consists of two dye lasers, two amplifier stages and a gated saturable absorber (GSA) placed between the amplifiers. The dye lasers sharpen the leading edge of the laser pulse while the GSA cuts the trailing edge of the pulses. The combined pulse shaping of the dye lasers, amplifiers and GSA results in a ~ 8 ps pulse centred at 365 nm. These pulses are used for pumping the DFDL. The DFDL consists of a coarse transmission grating, a microscope objective and a special dye cell with the active medium (Cournarin 307 dye). The DFDL is a special set-up allowing generation of short, femtosecond pulses from a seeding pulse of longer pulse duration. The mechanism works via imaging an interference pattern of a seeding laser pulse onto the wall of the dye cell via a grating. The output wavelength of the DFDL is set to twice the KrF wavelength (496 nm). The output of the DFDL is again amplified via a two-stage amplifier, separated by a saturable absorber and frequency doubled by a Beta-Barium Borate (BBO) crystal to yield pico- or femtosecond seeding pulses of 248 nm wavelength. This seeding pulse pumps the second cavity of the EMG 150 laser filled with KrF, via a double pass arrangement shown in Figure 2.2(b), yielding pulse energies in the range 10-15 mJ with pulse length 450 fs. 5 ps laser pulses can also be generated by insertion of a multiple reflection etalon in the dye laser set-up.

In both cases the output power was recorded by two different means. The output power was recorded via a beam splitter and power detector arrangement built into the laser housing, and measured independently using a Joule stick or a power monitor. To allow fine adjustment of the laser output into the vacuum chamber the laser beam was directed onto the target via two highly reflective mirrors held in kinematic mounts.
2.2. Vacuum chamber

The vacuum chamber for the ArF work consists of a cylindrical stainless steel vessel with internal diameter of 260 mm and height of 160 mm. The basal plane of the chamber is mounted on the table and pumped by a 100 mm turbomolecular pump (Leybold Turbotronic NTL59/369) backed by a two stage rotary pump (Leybold Trivac). The pumping system could be isolated from the vacuum chamber via a 'butterfly' valve. The top of the vacuum chamber consists of a large flange that can be removed to access the chamber. Ten additional flanges are connected on the walls of the vacuum chamber to mount pressure gauges, a (reactive) gas inlet, electrical feed-throughs, substrate and target holders, backing pump (rotary), laser input window and the Faraday Cup/Quadrupole Mass Spectrometer (QMS) assemblies. The vacuum chamber assembly for the KrF laser ablation studies was slightly different, primarily with regard to the means of mounting and using the optical emission assembly and CCD array. This will be described at the appropriate point later in this chapter.

The pressure in the chamber used for the ArF laser ablation studies is measured by Pirani and Penning gauges (Edwards) and a baratron (MKS). The range of pressures measurable with this assembly is $5 \times 10^{-8}$ to 10 Torr. A typical base pressure maintained in the ablation chamber was $\sim 10^{-6}$ Torr. Throughout this work, ablation/deposition conditions described as vacuum will refer to a base pressure of $\sim 10^{-6}$ Torr. When required, a (reactive) background gas was introduced into the chamber via a Mass Flow Controller (MFC, Tylan) up to pressures of $\sim 50$ mTorr. Pressure readings were obtained from the Pirani gauge and the baratron. Typical gas flows were $\sim 5$ sccm. This assembly allowed a controllable and precise gas flow and enabled stable and reproducible pressures over typical deposition times of 15 minutes.

The top flange of the vacuum chamber for the ArF work also supports a large rectangular quartz window ($90 \times 45$ mm$^2$) thus allowing for measurements of optical emission from the plasma plume. The optical emission assembly for the KrF work is mounted so as to view through one of the side flanges, equipped with a quartz window. The CCD camera imaging was performed either through a polished poly-methyl-methacrylate (PMMA) top flange (ArF work) or via a window in the horizontal plane at the height of the target holder (KrF work). These differences are shown in Figure 2.3.
Chapter 2: Experimental Techniques

Figure 2.3: The two different set-ups used to monitor OES in the laser ablation experiments using (a) ArF and, (b) KrF laser irradiation.

The entrance window through which the laser beam passes consists of a 50 mm diameter quartz flat in both ablation chambers. During laser ablation, material is unavoidably deposited onto these windows. This results in some attenuation of the incoming laser light as the thickness of the film deposited on the entrance window increases with time, which hampers estimation of the laser fluence reaching the target surface. Because of this, the laser window is replaced after every 15 minutes (9000 shots) of laser operation during deposition. In the case of laser ablation studies the windows were exchanged after ~3000 shots to ensure a constant, measurable laser fluence. The film deposited on the laser window was removed afterwards, by heating in air in a Bunsen flame in the case of deposition of Diamond Like Carbon (DLC) or by placing them in ‘Aqua Regia’ in the case of metal or zinc oxide deposition.

2.3. Target Materials and Holder

2.3.1. Target materials

The target materials used in this thesis are 2 inch diameter disks of Highly Oriented Pyrolytic Graphite (HOPG, Poco Graphite Inc., DFP-3-2 grade) and high purity ZnO (99.99 % pure, Testbourne). For the doped ZnO studies, sintered disks consisting of 5%
Al or Ga and 95% ZnO (Testbourne) were used. The ablation of metal was performed with commercially available 2 inch diameter Cu or Al disks.

### 2.3.2. Target holder

Two different target holders were used in the ArF laser ablation studies. The first assembly consists of a rotating target (typically 1 rpm) directed at an angle of 45° with the incoming laser beam. It is rotated by a stepper motor mounted on the outside of the vacuum chamber. The rotation speed is chosen to be fast enough to provide a fresh target surface for every shot, although on typical deposition times (15 minutes) every spot on the ablation track is used 15 times, causing groove formation in the target. A drawback with this arrangement is that only a very small part of the target surface is used for ablation (only the laser track) and, since the target surface is polished after 15 minutes of ablation to reduce track formation, a large part of the target surface is removed without being used.

![Figure 2.4: A photograph of the (x,y) translation stage used in the ArF laser ablation.](image-url)
The second assembly houses the target in an (x, y) translation stage (shown in Figure 2.4). The stepper motors that drive this assembly are mounted in the vacuum. In this assembly the target is stepped in both the x and y directions while the laser interaction spot is held stationary. The advantages on this set-up are (i) that the target surface can be ablated much more efficiently and for a longer time duration without groove formation and (ii) that the complete assembly can be rotated (about the vertical axis) relative to the incoming laser beam, thus giving a greater versatility. One of the main disadvantages is that operating the stepper motors in vacuum can cause them to overheat at longer time scales, because of the poor temperature conduction in high vacuum, leading to assembly failure. Introduction of stepper motors in vacuum also increases the introduction of contaminants (oils), degrading the vacuum conditions and necessitating longer pumping times.

2.4. Plasma Detection Equipment

The laser ablation event at high fluences (typical > 1 J/cm²) produces a time evolving plasma cloud. This plasma can be studied by a number of different techniques. The easiest and most common techniques for analysing the plasma are optical emission spectroscopy and electrical probes. The optical emission arising from the plasma can be viewed time independently or time dependently using a quartz fibre to couple the emitted light into a monochromator/photomultiplier assembly or by time gated CCD imaging. The total ion and electron current in the plasma can be detected by electrical probes and can be studied time dependently using a Langmuir probe or a Faraday Cup assembly. In addition, the plasma can be studied by Mass Spectrometry. This technique allows for mass separation of the detected particles and for detection of the neutral particles in the plasma. In addition, the intensity and temporal profile of the laser pulse can be studied after passage through the ablation plasma, revealing any attenuation effects of the laser light by the expanding plasma. This effect is studied using a special set-up discussed below.
2.4.1. Optical Emission Spectroscopy

Optical emission from the plasma formed by the incident fluences used in the present work are clearly visible by eye. This emission can be studied with the assembly shown in Figure 2.5. The optical emission arising from the detection column in the plasma is focused by a lens through an iris onto the front end of a quartz fibre optic bundle (Oriel). The rear end of the fibre optic abuts the entrance slit of one of the two monochromators used in this study and described below. The input end of the fibre optic is circular (3 mm diameter) and the output of the fibre is a $1 \times 7$ mm$^2$ rectangular slit to match the entrance slits of the monochromators. The viewing column in the focal point of the lens, aligned so as to sample the plasma plume along the target surface normal, has an estimated diameter of 2 mm, indicating the minimal experimental error on the spatial measurements made with this assembly. The whole assembly can be translated in two orthogonal directions in the horizontal plane (see Figure 2.5) to provide spatially resolved measurements.

![Figure 2.5: Experimental assembly for wavelength dispersed optical emission spectroscopy.](image)
For the ArF work two monochromators were employed. One was a 12.5 cm monochromator, equipped with a 600 lines/mm ruled grating and a UV extended Instaspec IV CCD array detector. With this arrangement, time integrated, low-resolution (0.9 nm) dispersed emission spectra over a wavelength scale of 225-1025 nm could be recorded. Synchronisation of the detection system with the laser ablation event and summing over a number (typically 30-250) of shots obviously greatly enhances the signal to noise ratio of the measured spectra. The spectra are wavelength calibrated by recording the dispersed emission spectrum of the room lights, which contains strong mercury emission lines. The spectra are presented uncorrected for the wavelength dependent quantum efficiency of the grating and the CCD array detector unless stated otherwise. The overall detection sensitivity peaks at ~620 nm and is four times lower at the two extremes of the wavelength range investigated (i.e. 225 and 1025 nm).3

The second monochromator is a 0.5 m Spex 1870 equipped with a 2400 lines/mm holographic grating. Photons transmitted through the monochromator are detected using a red sensitive fast Photo Multiplier Tube (PMT). Wavelength calibration of this spectrometer involved recording and measurement of well-documented Ne emission lines from a neon hollow cathode lamp. This monochromator/PMT assembly allows measurement of the intensity associated with a specific emission feature as it expands through the viewing column, simply by positioning the grating of the monochromator so as to transmit the wavelength of the emission line of interest and monitoring the transient emission signal as a function of time after the laser pulse is incident on the target. The entrance slit width to the monochromator is user-selectable and was chosen to be 400 μm. The output of the PMT is directed to a digital oscilloscope (LeCroy 9361, 2.5 GHz sample rate) and is stored via a GPIB interface on a PC. Zero time was established accurately by monitoring the scattered radiation from the iris in the beam line immediately in front of the entrance window of the ablation chamber. These transient signals are summed over 30-250 shots (depending on the intensity of the line) to enhance the signal to noise ratio.
2.4.2. CCD camera imaging

Two different set-ups were used for the CCD camera imaging studies. The first consisted of a CCD camera mounted on the top flange of the chamber and was used in Chapter 4 (ArF work). The second consisted of a CCD camera mounted on the side of the chamber so as to view in the horizontal plane. This was used in Chapter 6 (KrF work). The two different set-ups were shown schematically in Figure 2.3. The i-CCD camera used in the set-up shown in Figure 2.3(a) and discussed in Chapter 4 uses a Photonic Science camera equipped with a time gated image intensifier. The typical time gate used was 0.1 µs. The camera is mounted in the vertical plane in the laboratory frame. A Pentax 25 mm TV lens imaged the ablation plume onto the CCD array yielding a squashed 2-D (xy) projection of the full 3-D plume of emitting particles. The set-up in Figure 2.3(b) uses an intensified and gated CCD array (iStar 720D Andor Technology) as an i-CCD camera. The camera was mounted in the horizontal plane in the laboratory frame. The image was projected onto the 1024 x 256 CCD array by a confocal lens with 20 cm focal length, in a set-up that gave a 2:1 magnification.

Images recorded were either of the total emission or of selected emission lines, by viewing through appropriate optical filters. The intensifier was triggered by the signal of a fast photodiode monitoring scattered radiation from the ablation laser pulse.

2.4.3. Langmuir Probes

Langmuir probes are one of the simplest techniques for obtaining information about the ions in a plasma. They consist of an electrode of known area inserted in the plasma and connected electrically to a variable-voltage power supply (see Figure 2.6). This power supply is in turn grounded to a reference electrode inserted in the plasma. The reference electrode in the case of a single Langmuir Probe is much larger than the probe itself and typically consists of the chamber walls or any other convenient conducting surface in contact with the plasma. This apparently simple experimental technique is associated with rather complicated theories that are needed to explain the current-
voltage behaviour of these probes in a plasma.\textsuperscript{4-6} Thus we start by providing theoretical background to the technique.

2.4.3.1. Theory of Langmuir Probes

The probe current is dependent on the potential imposed on the probe. A typical current-voltage plot is shown in Figure 2.7. This characteristic is normally determined by the plasma properties in the immediate vicinity of the probe.\textsuperscript{4-6} The general shape of the $I-V$ characteristic can be divided into three parts. When the probe is biased positively with respect to the local plasma potential the flux of particles reaching the probe will consist of carriers of negative charge (normally electrons). This region is called the electron accelerating region and is labelled III in Figure 2.7. These electrons will be collected from a region called the sheath, which is the region close to the probe surface where the potential exerted by the probe is not shielded by the plasma. When the probe is biased at a potential slightly smaller than the plasma potential only particles with enough energy to overcome the potential barrier will be collected. This region (region II in Figure 2.7) is called the electron retarding region. The third region is accessed when the probe is biased increasingly negative relative to the plasma potential. In this region (region I in Figure 2.7) only positive ions will reach the probe. This region is called the ion saturation region. The governing theories applicable to these three regions in the $I-V$ plot are discussed in the remainder of this section.
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The electron-retarding region (region II) is the easiest to describe and will be discussed first. In this region the probe actually acts as an energy selector, collecting only those electrons which have large enough kinetic energies to overcome the potential barrier. If the electron distribution is in local thermal equilibrium, the electron energy distribution function can be assumed to be Maxwellian and the current drawn in this regime follows the relation

$$I_e = n_e A_p \left( \frac{k T_e}{2 \pi m_e} \right)^{1/2} \exp \left( \frac{e(V - V_p)}{k T_e} \right).$$

(2.8)

where $I_e$ is the electron current, $n_e$ the electron number density, $e$ the electron charge, $A_p$ the probe area, $k$ the Boltzmann constant, $T_e$ the electron temperature and $m_e$ the electron mass. The gradient of a plot of $\ln[I_e]$ versus the applied voltage, $V$, yields the electron temperature and, given knowledge of the electron current at the plasma potential, substitution of $T_e$ in Equation (2.8) yields to the electron number density.

The electron acceleration region (III) is governed by the orbital motion theory, and an expression for the electron current in this region can be derived as follows: consider a point charge at a bias potential $V_b$, separated from an electron with charge $e$ by a

Figure 2.7: Typical current voltage plot, $V_p$ represents the plasma potential.
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distance $r_0$ where the potential is $V_p$. Assume that the electron has a forward trajectory.
with velocity $v_0$ and impact parameter $p$ as defined in Figure 2.8.

![Figure 2.8: Schematic of the input for the orbital motion theory.](image)

The total kinetic energy $T$ of the particle at any time during its trajectory is given by:

$$T = \frac{1}{2} m \left[ v^2 + r^2 \left( \frac{d\psi}{dt} \right)^2 \right]$$  \hspace{1cm} (2.9)

where the two terms on the right hand side of expression (2.9) are, respectively, the translational and the rotational parts of the total kinetic energy. Given that (conservation of angular momentum):

$$\frac{d\psi}{dt} = \frac{p v_0}{r^2}$$  \hspace{1cm} (2.10)

we can rewrite the expression (2.9) as:

$$T = \frac{1}{2} m v^2 + T_0 \frac{p^2}{r^2}$$  \hspace{1cm} (2.11)

Given equation (2.11) we can rewrite the total energy of the system as:
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\[ E_T = \frac{1}{2} mv_0^2 - eV_p = \frac{1}{2} mv^2 + T_0 \frac{p^2}{r^2} - eV \]  \hspace{1cm} (2.12)

At the point of closest distance to the probe \((r_c)\), the translational kinetic energy is totally converted into centrifugal energy \((v = 0)\), thus the total energy expression (2.12) can be rewritten as:

\[ \frac{1}{2} mv_0^2 - eV_p = T_0 \frac{p^2}{r_c^2} - eV_c \]  \hspace{1cm} (2.13)

Rearranging expression (2.13) gives:

\[ p = r_c \left[ \frac{e(V_c - V_p)}{T_0} \right]^{1/2} \]  \hspace{1cm} (2.14)

Taking \(r_c\) as the probe radius \(a\), any particle with \(p < a[1+(V_c-V_p)/T_0]^{1/2}=p_0\) will be collected. The expression for the current collected by a cylindrical probe given a Maxwellian electron velocity distribution can also be derived (analogous to (2.8)). It takes the form:

\[ I_c = n_e e A_p \left( \frac{kT_e}{2\pi m_e} \right)^{1/2} \left[ \frac{2}{\sqrt{\pi}} \left( 1 - \frac{e(V - V_p)}{kT_e} \right)^{1/2} \right] \]  \hspace{1cm} (2.15)

Plotting the square of the electron current against the probe voltage yields a straight line, the gradient of which provides a measure of \((n_e)^2\).

The ion saturation current region (1) is a more difficult region to describe. The amount of ion current is governed by the Bohm criterion, since the ion temperature is much lower than the electron temperature in the plasmas under consideration. The Bohm criterion states that the ion velocity must acquire a positive (towards the probe) velocity at the plasma sheet edge even when the ions have very low temperatures. This velocity is provided by the existence of a “pre-sheet” potential drop that occurs at long
distances in the plasma. The ion current is thus dependent on the electron temperature and is given by:

\[ I_\text{i} = 0.6n_{i\infty}eS\sqrt{\frac{T_e}{m_i}} \]  \hspace{1cm} (2.16)

where \( n_{i\infty} \) is the unperturbed (by the electric field of the probe) ion density and \( S \) is the surface area of the probe.

Since the ion current is dependent on the electron temperature there is no easy way to deconvolute the total signal into the ion density and the electron temperature without independent measurement of one of the parameters.

The above expressions are strictly only valid in collisionless sheath conditions (i.e. when the mean free path \( \lambda > \) sheath dimensions). Higher order corrections have to be included in the expressions in situations where collisions occur within the plasma sheath.

2.4.3.2. Langmuir probes in laser ablation

Most electrostatic probes used in ablation plasmas are ion probes.\(^7\) Ion probes have the advantage that data can be acquired faster; most ion probe work is performed at one set voltage while, with a Langmuir probe assembly, the voltage has to be swept over a range of voltages to obtain information about the electron distribution. As can be seen from equation (2.16) the use of cylindrical ion probes close to the target can be problematic if one wants to deconvolute the ion density from the electron temperature. A better method for measuring ion densities involves use of a Faraday Cup assembly, at larger distances from the target, where the particles propagate essentially in a free flight regime.

Langmuir probes are employed in laser ablation studies, particularly to obtain more information about plasma parameters, such as the electron density and temperature and, more importantly, to learn about the transient characteristics of the plume. Absolute measurements of the electron density and the electron temperature are less important since their values depend strongly on the distance and time delay of measurement.
Relative measurements of the density transients suffice to provide a TOF distribution from which the velocity distribution of the electrons can be derived.

The theory associated with the use of Langmuir Probes in laser ablation plasmas has been studied in depth by Weaver et al. Since the standard Langmuir probe theories generally apply to static plasmas some specific considerations have to be taken into account. Under the ablation conditions prevailing in their study—which are very comparable with the conditions used in this work—it has been shown that the Langmuir probes operate under collisionless sheath conditions. Under these conditions, it can be shown that the I-V characteristics of the probe are well approximated by those of a static, non-flowing plasma, provided the root mean square thermal velocity of the electrons in the plasma is at least three times greater than the local flow velocity. Given a local flow velocity and the standard conditions during laser ablation, the electron temperature has to be greater than 0.04 eV. This condition is easily satisfied during laser ablation, the values derived from the study of Weaver et al. yielded values for the electron temperature of >1 eV for the moderate fluence (5 J/cm²) laser ablation of copper.

2.4.3.3. Specifics of the Langmuir probe

The Langmuir probe assembly consists of a Tungsten wire, 125 μm in diameter and 8 mm in length, supported by a glass sleeve (see Figure 2.6). The wire can be biased at voltages in the range of -30 to 30 V, relative to the target and the vacuum chamber, with a stabilised power supply coupled to an electrical circuit that enables the probe to be maintained at a constant bias while passing the transient current due to charged material in the ablation plume to the oscilloscope. Great care was taken to prevent the probe feed wires being exposed to the plasma since this will contribute to the measured probe signal. To ensure a clean probe surface, the probe wire is replaced every ~10,000 shots, although no signal attenuation due to material deposition on the probe was observed during the experiments.

The output of the Langmuir probes was directed to a digital oscilloscope (LeCroy 9361, 2.5 GHz sampling rate) and then, via a GPIB interface, to a PC for storage and data processing. Zero time was established by monitoring the signal from a fast photodiode positioned so as to detect a fraction of the laser output pulse.
2.4.4. Faraday Cup

A second way to study the ions in the plasma involves use of a Faraday Cup assembly. This detector consists of a polished stainless steel plate, 15 mm in diameter, mounted 4 mm behind an annulus supported, 85% transmitting, grounded tungsten mesh. The front face of the plate was positioned at a distance $d = 421.7$ mm from the focal spot, along the surface normal (thus the plasma propagation axis). The stainless steel flat was maintained at a voltage of $-20$ V to repel the electrons in the plasma, while the mesh was held at ground potential. The plasma was measured behind a 2 mm pinhole to enable higher resolution angular measurements. A schematic of the set-up is given in Figure 2.9.

![Figure 2.9: Faraday Cup assembly](image)

The Faraday Cup was used in combination with the target (x,y) translation stage. This set-up can also be used to provide information about the angular distribution since this translation stage can be rotated around the laser interaction region. Rotating the target will have implications on the laser footprint on the target and on the interaction of the laser beam with the ablation plume (we show later that the radial distribution of the flux in the ablation plume can be described as a $\cos^8\theta$ relationship, where $\theta$ is the polar angle defined relative to the surface normal). The influence of these parameters on the
incident laser fluence is assumed to be small for small \((\theta \pm 20°)\) angular variations. The angular distribution obtained by these measurements is peaked along the surface normal assuring this assumption, as will be described in Chapter 4.

2.4.5. Mass Spectrometer

This project also involved commissioning and evaluating a state of the art Quadrupole Mass Spectrometer (QMS, HIDEN, HAS-5PL-4353). A short introduction to the operation of this instrument is given in this paragraph. A more detailed characterisation of this apparatus is presented in Appendix 2. The internal structure of the mass spectrometer is given in Figure 2.10. It consists of 5 key parts, namely the extraction region, the source region, the electrostatic analysis (ESA) region, the quadrupole mass filter (QMF) and the detection region incorporating a secondary electron multiplier (SEM).

![Figure 2.10: Schematic of the electrostatic lenses in the mass spectrometer. ESA stands for the electrostatic analyser, QMF stands for the quadrupole mass filter and SEM stands for the secondary electron multiplier.](image)

The extraction region consists of two electrostatic lenses, the extractor lens and a lens to focus the ions into the source region. The extractor lens is mainly used to extract ions out of a stationary or thermal plasma and is (because of the high directionality of the ablation plasma) of minor importance for laser ablation plasmas. The second
focusing lens (lens I in Figure 2.10) plays a more important role during operation of the mass spectrometer. This will be discussed in greater detail in Appendix 2. Since this region precedes the source region of the QMS, the electric fields generated by these extractor lenses only affect the trajectories of the ions, not the neutrals, entering the QMS.

The source region consists of a tuneable electron impact ionisation source and a focusing lens. In this region neutral particles can be ionised by electron impact and focused into the electrostatic analysis region.

The electrostatic analysis region is the energy filter of the mass spectrometer. It consists of a field free region which is on a variable potential. After the field free region only the particles with a given kinetic energy (20 eV) will be deflected through the necessary 45° to enter the centre axis of the subsequent quadrupole mass filter and thus reach the detector. Particles with other kinetic energies will not be deflected through the ideal 45° angle and will subsequently not be detected. Energy selection is obtained by changing the voltage on the field free region; by ramping this voltage particles with different initial kinetic energies will be progressively accelerated to the required kinetic energy for optimal deflection towards the detector, thus allowing measurement of a kinetic energy distribution. Unfortunately this set-up for energy selection exhibits a number of problems when applied to laser ablation studies, as will be discussed in Appendix 2.

The Quadrupole Mass Analyser is a standard quadrupole mass filter and the detector consists of a secondary electron multiplier.

### 2.4.6. Jacobian Transformation

An obtained TOF profile can be transformed into its corresponding velocity distribution by a non-linear Jacobian transformation. In practice, this can be done by rebinning the original TOF signal, which is recorded in a number of equal time increments (or bins). Thus the total signal in a given time bin has to be adjusted, by dividing by the bin length, while maintaining the same total signal, in order to convert the horizontal axes of a TOF profile (time) to a velocity distribution (velocity), since these are connected in a non-linear way \( v = \frac{d l}{l} \). To obtain the same total signal for the TOF and velocity distribution the horizontal axis of the TOF distribution is first
converted into a non-linear velocity scale. The amount of signal in every bin is then redistributed in a linear velocity scale, by considering the degree of mutual overlap between the nonlinear and linear bins. This procedure is of course easily implemented in a computer code, which has been written in FORTRAN77. The correctness of the routine was monitored by both calculating the mean velocity for the TOF and velocity converted distributions and by comparing the total amount of signal before and after conversion. Both distributions have to give the same value for both of these quantities, since neither should be affected by the transformation.

2.4.7. Determination of the attenuation of the laser light by the ablation plasma

The set-up for measuring attenuation of the laser light by the ablation plume is given in Figure 2.11. The output of an excimer laser (Lambda Physik. Compex 201) operating on ArF (193 nm, 10 Hz repetition rate, output energy ≤ 300 mJ pulse⁻¹) was steered using two (or three) dichroic mirrors and focused (20 cm focal length lens) so as to be incident, along the surface normal, on a graphite target located in a stainless steel vacuum chamber maintained at ~10⁻⁶ Torr. The target (0.75 mm thickness) has a small hole mechanically drilled through the surface so as to transmit a fraction of the laser light (for eventual detection). The transmitted light is attenuated further by reflection off 2 quartz flats (reflection ~10 % in each case) and steered through a monochromator set so as to transmit only 193 nm light before detection on a fast photodiode. The current on the photodiode is recorded on a digital oscilloscope (50 Ω terminated, LeCroy 9361) and then transferred via a GPIB interface, to the PC for storage and subsequent data processing. Attenuation of the light by reflection off the quartz flats was necessary so as not to saturate the photodiode.
2.5. Film deposition

Deposition runs were typically performed at fluences between 10 and 25 J/cm² dependent on the material to be deposited. Deposition times ranged between 2 and 15 minutes at a laser frequency of 10 Hz, and the substrates were mounted at a distance of 4 to 7.5 cm from the target. The background pressure for deposition is dependent on the film material sought and ranges between high vacuum (10⁻⁶ Torr) and 10 mTorr.

The substrate material was typically Si(100) wafer cut into pieces of 1 cm² surface area. UV-visible absorption spectroscopy measurements required film growth on fused quartz substrates also. The use of clean substrates is of the utmost importance if a coherent film is to be obtained. Both the quartz and silicon substrates were cleaned with ‘aqua regia’ and methanol before deposition.

The substrates were mounted either on a carousel, on which four substrates could be mounted simultaneously, or on a heated substrate holder. During deposition with the former arrangement, exposure of just one substrate to the ablation flux can be assured by rotating a shield associated with the carousel so as to mask all bar the one substrate of interest. This enables deposition of four different films without opening the vacuum chamber. The substrate heater consists of a 100 W halogen light bulb (8 A, 12.5 V), in
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contact with a small copper substrate holder on which one substrate could be attached. This set-up enables substrate temperatures \( \leq 500^\circ C \) to be reached, as measured with a calibrated thermocouple.

2.6. Film analysis techniques

2.6.1. Raman Spectrometry and Photoluminescence spectroscopy

Laser Raman spectroscopy (LRS) provides information on the phonon structure of the deposited films. As discussed later, this phonon structure is critically sensitive to the quality of the deposited films. Photoluminescence (PL) spectroscopy provides information about the electronic structure of the material - another property that is also highly dependent on the quality of the films. Both of the analysis techniques can be used as tests of the quality of deposited films.

LRS was performed at a number of excitation wavelengths, 488 nm laser excitation was achieved using by an \( \text{Ar}^+ \) laser (Spectra Physics 12000) coupled to a Renishaw Ramanoscope (G52836). This provides \( \sim 4 \) mW on the sample in a spot diameter of \( \sim 3 - 4 \) \( \mu \)m. The same set-up was used to record spectra following excitation at the other \( \text{Ar}^+ \) laser line (514 nm), in this case with up to 20 mW power focused into a \( \sim 1 \) \( \mu \)m spot. Spectra taken at 325 nm were obtained using another Renishaw Ramanscope (G92360) and operating with a Kimion K series HeCd laser which provided \( \sim 3 \) mW on the sample in a spot size of \( \sim 2 \) \( \mu \)m.

Each spectrum is typically an accumulation of 10 scans and is calibrated by the Si(100) peak at 520 cm\(^{-1}\). Photoluminiscence was obtained with the 325 nm excitation wavelength, with all the procedures the same as for the Raman spectrometry.
2.6.2. Scanning and Transmission Electron Microscopy

The surface structure and the thickness of the deposited films can be imaged by scanning electron microscopy (SEM), while the nanoscale structure and crystallinity of the material can be investigated by TEM.

Scanning electron microscopy was performed with a Jeol SEM 5600 LV system, while TEM used a Jeol TEM 2010 instrument, and high-resolution images were obtained using a Jeol SEM 6330 FEG. For the higher resolution images it was necessary to first coat the films with platinum in a sputter source so as to obtain better contrast. The microscopes also have the facility for EDX (Energy Dispersed X-ray) spectroscopy, which can provide information on the surface composition both of the target materials and the deposited films. These X-rays are generated by the high-energy electron (10-20 keV) impact on the surface of interest and are detected using a Si.Li detector, calibrated with respect to cobalt metal emission (6.925 keV). Quantitative analysis was carried out by using the Oxford link Isis system.

Films for TEM analysis were deposited on mica pre-coated by a sputtered DLC film and post processed to yield stand alone thin films. For this application the films were typically deposited for 2 minutes. It was possible to perform planar TEM on these films.

2.6.3. Ultra-Violet and Visible Spectrometry

The Ultra-Violet/Visible (UV-VIS) spectrum of a material provides information about its optical properties, which are directly related to its electronic properties. It provides information on the optical band gap, sub-band gap absorption etc. and can also be used as an indicator of the quality of the deposited films.

UV-VIS absorption spectra were recorded on a Perkin Elmer Lambda Bio 10. The radiation sources in this spectrometer are deuterium and halogen lamps (lamp crossover at 326 nm) giving a full range of 200-900 nm, an accuracy of ± 0.5 nm and a spectral bandwidth of 2 nm. Absorbances of films grown on quartz substrates are taken against a background reading of a blank quartz film using UV Winlab™ software on a PC.
2.6.4. X-ray diffraction

X-ray diffraction gives an insight into the crystalline structure of a given material, since the interplanar spacing in regular crystals is of the order of the wavelength of X-ray radiation. Irradiating a crystal with a collimated and mono-energetic X-ray source gives rise to constructive and destructive interference via scattering of the X-rays of the crystal planes. Given the situation in Figure 2.12, where the crystal planes of the sample make an angle of \( \theta \) in respect with the X-Ray source and the detector is situated at an angle of \( 2\theta \) with the X-Ray source. To obtain constructive interference the path length A-B-C has to be equal to an integer multiple of the incident wavelength. This leads to the formulation of Bragg's law (2.17):

\[
 n\lambda = 2d \sin \theta
\]  

(2.17)

Figure 2.12: Figure explaining the Bragg equation.

where \( \lambda \) is the wavelength of the X-rays, \( d \) is the interlattice spacing, \( \theta \) is the incident angle and \( n \) is an integer. Different crystal planes will have different diffraction angles. In this way X-ray diffraction gives essential insight in the alignment of the film. Deviations from the ideal refraction angle indicate perturbations of the interlattice spacing. Such deviations can be caused by internal stresses (smaller \( d \)) or deviations from the ideal stoichiometry. A further determination of the crystal structure is provided by recording rocking curves of the samples. Obtaining a rocking curve
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involves rotating the target while the X-ray source is kept stationary. Rocking curves can give a measure of the misalignment of the individual crystallites in the film.

X-ray diffraction spectra were measured on films grown on Si(100) and quartz substrates using a Bede D1 system and an X-ray wavelength of 1.54056 Å (Copper Kα). Spectra were calibrated with respect to the (100) silicon substrate peak.

2.6.5. Atomic Force Microscopy

With Atomic Force Microscopy (AFM) the surface of a material is probed with an atomically sharp tip, which is attached to a flexible cantilever. The cantilever deforms under repulsive interactions between the surface and tip atoms. The cantilever tips are usually made from Si₃N₄ and have a 5 nm surface area. The deformation of the cantilever (which obeys Hooke’s law) can be directly measured by the displacement of a laser beam reflected from it onto a 2-D photodiode array.

There are two contact methods of measuring the surface topography, namely the direct contact mode and the tapping mode. In the direct contact mode, the height profiles at a constant force (using a feedback system) or the force profiles at a constant height are measured by the probe. The main problem with the method is that the tip can drag over the surface and the lateral forces can distort the nascent surface structure. The problem of the direct contact method is overcome in the tapping mode by oscillating the cantilever at its resonant frequency, just above the surface. In one of part of the cycle, the tip briefly interacts with the interatomic force field. This brief contact drastically reduces the effect of the lateral force. Monitoring the phase difference between the driving oscillator and the oscillation measured by the 2D detectors offers a route to information on the viscoelastic and stiffness properties of the surface.¹⁰ When the material surface is rastered relative to the probe, the phase difference plot can provide information about the surface roughness since the strength of the force between the cantilever and the surface drops rapidly with increasing distance.

AFM analysis was performed by a Digital Instrument NanoScope on films grown on Si(100). The probe resonates at 3.988 Hz and takes 521 samples per analysis.
2.6.6. Field emission testing

The Field Emission of DLC films was investigated via an in house Field Emission test kit.\textsuperscript{11} This consists of a diode arrangement, mounted in a high vacuum chamber (10\textsuperscript{-7} Torr). DLC samples are placed onto an earthed sample holder (cathode) and the electrical contact of the film surface with ground was ensured via the application of silver dag paint. The anode consisted of a copper tip. The cathode-anode separation was adjustable, by a precision micrometer, and was typically in between 20-60 \mu m. The bias voltage was provided and controlled by a high voltage DC power supply, and the current was measured with a sensitive multimeter (capable of measuring currents of 1 pA). To obtain the \textit{I/V}-curves the bias voltage was ramped up and down (maximum voltage = 3.5 kV) while the resulting current was measured.

2.7. References

Chapter 3: General Theory

3. General Theory

This general theory chapter is divided into three parts. The first part focuses on a theoretical description of the laser ablation process and is based mainly on thermodynamic and gas dynamic concepts. This is followed by some discussion of the studied materials (Diamond Like Carbon (DLC) and Zinc Oxide (ZnO)). The final section provides an introduction to the theoretical description of periodic solid state structures by \textit{ab initio} methods, focusing particularly on the bulk crystal and the surface structure of ZnO.

3.1. Laser Ablation

Laser ablation is a macroscopic process, which is difficult to approximate theoretically, mainly because of the extreme conditions that are typically involved. The high photon flux provides essentially instantaneous heating of the material, sometimes to temperatures near the critical point. The material reacts to this temperature increase by evaporation. The particles in the dense emitted gas cloud can also interact with the laser photons, which heats the gas cloud rapidly so that it becomes a plasma. This plasma cloud obtains a high kinetic energy and a high degree of ionisation in this process, which can have interesting implications for material deposition.

3.1.1. Laser interaction with solid material, and particle ejection

The interaction of a pulse of laser light with a solid material can be divided into two sub-categories, depending on the pulse duration. The difference between the two regimes can be explained as follows: laser-solid interactions with nanosecond or longer laser pulses are of sufficient duration to couple not only into the electronic, but also the vibrational wavefunction of the material (phonon relaxation times are typically $\sim 1 \text{ to } 5 \text{ ps}$), while for femto/picosecond pulses the duration of the excitation is too short to
couple directly into the vibrational wavefunction. Thus laser interactions with these different pulse durations can be expected to induce different ablation behaviours.

### 3.1.1.1. Nanosecond ablation

The discussion of nanosecond pulsed laser interaction with materials will focus on the ablation of crystalline solids. Polymer ablation is specifically excluded since their excitation with excimer (UV) lasers exhibits a clearly distinguishable photochemical component, which is attributable to the unique structure of polymers. The nanosecond ablation of crystalline solids shows very different behaviour and will be discussed in the following paragraphs.

At low fluences, typically around the laser ablation threshold, many of the crystalline solids show a non-thermal particle ejection behaviour when irradiated with visible and especially UV laser pulses. This has been observed in the case of Nd:YAG laser irradiation (at 266, 355 and even 532 nm) of metals and KrF (248 nm) irradiation of graphite and ZnO. The electronic excitation mechanism results in the ejection of high kinetic energy species, which cannot be explained by thermal evaporation. This behaviour is normally attributed either to excitation of surface plasmons or to (multiphoton) excitation of surface defects. At higher fluences, any such non-thermal effects decline in relative importance as the thermal evaporation starts to be the dominant mechanism for particle ejection.

At the typical fluences reported in this thesis (5-20 J/cm²) it is assumed that thermal conduction into the solid and consequent thermal evaporation is the predominant ejection mechanism. The equation governing this thermal ejection mechanism is the well known heat conduction equation:

\[
\rho(T)C_p(T) \frac{dT}{dt} = \frac{c^2}{z^2} \left( \kappa(T) \frac{dT}{dz} \right) + (1 - R) \alpha \ell(t) e^{-\alpha z}
\]  

where \( \rho \) is the density of the material, \( C_p \) is the heat capacity, \( T \) is the temperature, \( t \) is the time, \( z \) is the depth within the material, \( \kappa \) is the heat conductivity, \( R \) is the material reflectivity, \( \alpha \) is the absorption coefficient of the material and \( \ell \) is the intensity of the
laser irradiation. It is important to note that the absorption coefficient is actually the only wavelength dependent term in equation (3.1). The absorption coefficient for most known materials rises with increasing photon energy, which explains the preferential usage of UV-lasers for ablation. A high photon absorption coefficient equates to a smaller laser-material interaction region (recall the exponential term in equation (3.1)) and thus to a more efficient coupling of the laser light into the surface region of the target. As a direct consequence laser excitation with longer laser wavelengths yields a higher heat conduction into the bulk of the material, which is an energy loss process in competition with ablation.

This equation can be easily solved for different materials with a finite element calculation, and a number of studies have reported results obtained via finite element calculations for studying the laser melting process of graphite and silicon. The results obtained are in excellent agreement with the experimental data. Material ejection in such cases can be described in terms of thermally activated surface vaporisation, the rate of which is governed by the surface temperature $T_s$ (equation (3.2):

$$j(T_s) = \frac{\beta \rho_0}{\sqrt{2\pi A R T_s}} \exp \left[ \frac{\Delta H_{lv} (T_s - T_{lv})}{RT_s T_{lv}} \right]$$  

where $\beta$ is related to the sticking coefficient for surface atoms with atomic mass $A$. $R$ is the gas constant and the terms $H_{lv}$ and $T_{lv}$ are, respectively, the enthalpy and temperature of the liquid-vapour phase transition at an ambient pressure of $\rho_0$.

The material ejection mechanism and the total amount of flux ejected changes drastically when the fluence increases sufficiently to induce a process called phase explosion, or explosive boiling in the solid material. The phase explosion process occurs in solid targets at temperatures near to the thermodynamical critical temperature of the material, and can be described as a boiling induced by formation of homogeneous nucleation centres at a sufficiently high rate. The laser-induced melt relaxes explosively into a coexistent mixture of liquid droplets and vapour.

The nanosecond ablation of non-polymeric solids can be divided into three regimes, a low fluence regime that is correlated with non-thermal particle ejection, a higher fluence regime (normal deposition fluences) where the laser-material interaction and the particle ejection are well described by a predominantly thermal mechanism and
a high fluence limit where the solid reaches its critical temperature and undergoes phase explosion.

### 3.1.1.2. Femtosecond Ablation

The main model for explaining short laser pulse (< 1 ps) interaction with materials is the two temperature model developed by Anisimov et al.\textsuperscript{10} This model describes the temperature dynamics of the material irradiated by an ultra-short laser pulse. The model treats temperature conduction for the lattice and the electrons separately, as shown in equation (3.3). These two equations are coupled by a term that depends on the temperature difference between the two separate systems and an interaction constant, which reflects the strength of the electron-phonon coupling. It is important to note that, over short time scales, the source term (the laser light) appears only in the electron heat conduction equation.

\[
\rho(T_e) C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla (K_e \nabla T_e) - g(T_e - T_i) + S(z,t) \\
\rho(T_i) C_i(T_i) \frac{\partial T_i}{\partial t} = \nabla (K_i \nabla T_i) + g(T_e - T_i)
\]

\(\rho, \ C\) and \(K\) and \(T\) are respectively the density of the lattice, the heat capacities, the heat conductivities and the temperatures for the two subsystems (the electrons (given by subscript \(e\)) and the lattice (given by subscript \(l\)), \(g\) is the coupling constant and \(S\) is the laser source term.

In this model the laser light specifically heats up the electron distribution. At short time-scales (typically < 1 ps), only the electrons equilibrate, via electron-electron coupling, giving an immediate rise in the electron temperature, while the lattice remains at a low (ambient) temperature. The hot electrons start to diffuse within the target material because of the electron temperature gradient. The temperature of the lattice rises over a longer time-scale, which depends on the electron-phonon coupling strength (typical values over the range of 1-5 ps). After this time the electron and the lattice temperatures equilibrate and the system is governed by the standard heat equation. A schematic showing the processes on different time-scales is given in Figure 3.1.
Figure 3.1: Schematic of the processes and regimes in the Two-Temperature Model and the influence on the Fermi-Dirac distribution.

This model has been used extensively to explain melting thresholds for metals; and the results of such modelling show excellent agreement with experiment. The melting behaviour of semiconductors and graphite under short, intense laser pulse irradiation has also been subject to a number of experimental studies, but these all indicate that melting behaviour in these systems occurs much faster than the typical time-scale implied by the two-temperature model.

For silicon, the ultra fast transition between an ordered and disordered phase was studied by means of femtosecond time resolved measurements of the optical reflectivity and the second order optical susceptibility following irradiation with 60-100 fs titanium-sapphire laser pulses. The observed changes in optical properties are consistent with a two-step model involving an initial excitation stage and a subsequent transition stage. The optical properties during the excitation stage are determined by the
strong electronic excitation within the material, in particular, by the properties of a dense electron-hole plasma, while the optical properties of the transition stage are governed by the transformation of the crystalline solid to a metallic liquid, illustrated by an observed increase in the reflectivity. The time scale of the entire transformation is measured to be \( \sim 300 \) fs.

For graphite \(^5\), the short time scale laser heating process was studied by measuring the reflectivity of the target under 90 fs titanium-sapphire laser-radiation pulses. As in the case of silicon, an ultra-fast increase in reflectivity was observed. Again this transition to a more reflecting state is interpreted in terms of a transformation from the solid to a liquid metallic phase. The time-scale for the transition in graphite is estimated at \( \sim 90 \) fs, even shorter than in silicon.

The theoretical background for this process has been extensively studied by Silvestrelli et al. for both carbon \(^6\) and silicon \(^7,8\). These studies show that a very fast disordering of the lattice in these materials can occur at an ionic temperature considerably lower than the melting temperature of the lattice. The laser source term couples directly into the electronic distribution, promoting the electrons into highly excited states. Given this high level of electron excitation the effective ion-ion interactions can change drastically. At high fluences, a large fraction of the electrons are promoted into antibonding orbitals in both materials. The covalent bonds are weakened and the interatomic forces changed by this process. The system responds to the local differences in bonding interaction by 'melting' without any appreciable energy transfer between the excited ions and the lattice. This process has been termed 'plasma annealing' \(^9\) and can explain the fast transfer from the solid state into an electron-hole plasma. The time-scales of this disordering are calculated to be of the order of 90 fs for graphite and 200 fs for silicon.

The non-thermal nature of the ablation process on these short time-scales also has important consequences for the properties of the ablation plume. The ionic fraction in the ablation plume has been studied for the case of both graphite \(^20\) and titanium \(^21\) targets at a laser wavelength of \( \sim 800 \) nm and a pulse duration of \( \sim 100 \) fs by Time Of Flight (TOF) mass spectrometry. An example of the velocity distributions so derived is given in Figure 3.2. Double peak behaviour is clearly evident in this velocity distribution. The slower peak corresponds to a thermal cation distribution with a mean velocity of \( \sim 60 \) km/s, while the fast suprathermal peak travels with a velocity of \( \sim 240 \) km/s. Such plume splitting behaviour is explicable within the framework of the two-
temperature model. Since the electron distribution heats up, the hot electrons are free to escape to vacuum, while the cations remain relatively cold and stationary. Given the high electron density, the Debye length is of the order of a few Angstroms. Thus the cations do not feel the effect of the evolving electric field until the plasma expands and its density decreases to the extent that the Debye length becomes comparable to the plasma dimensions. Once the cations are subjected to the electric field, a fraction of them will accelerate to high velocities. This effect is charge dependent, so it is to be expected that more highly charged particles accelerate to higher velocities and are concentrated in the faster part of the suprathermal peak.

![Graph](image)

Figure 3.2: Velocity distribution of the ions, measured by a Time of Flight ion probe, arising from laser ablation of graphite at 800 nm using 100 fs laser pulses (Qian et al. 20).

### 3.1.2. Gas and plasma dynamics

At low fluences (i.e. near ablation threshold behaviour), the ejected particles undergo few substantial amount of collisions and their propagation through the vacuum can be approximated as a free flight. However, once more than about one atomic layer is ablated per laser shot this assumption ceases to be valid and gas dynamical effects start to play a significant role in the propagation of the ablation plume. 22

The gas dynamical equations can be written in the following forms, with the equations expressing the conservation of mass, momentum and energy:
\[
\frac{\partial \rho_v}{\partial t} = -\frac{\partial (\rho_v v)}{\partial x} \tag{3.4}
\]

\[
\frac{\partial \rho_v}{\partial t} = -\frac{\partial (p + \rho_v v^2)}{\partial x} \tag{3.5}
\]

\[
\frac{\partial \left[ \rho_v \left( e + \frac{v^2}{2} \right) \right]}{\partial t} = -\frac{\partial \left[ \rho_v v \left( e + \frac{p}{\rho_v} + \frac{v^2}{2} \right) \right]}{\partial x} + \alpha_v l_o(t) \exp(-\alpha_v x) - \varepsilon_{\text{rad}} \tag{3.6}
\]

where \( \rho_v, \rho_v e, v, p, \alpha_v \) and \( \varepsilon_{\text{rad}} \) denote the density, internal energy density, hydrodynamic velocity, pressure, the light absorption coefficient of the vapour and the radiative energy losses, respectively. These equations have to be completed by the equation of state relating the pressure to density and energy, namely the ideal gas law:

\[
p = (1 + \eta) \frac{\rho k T}{m} \tag{3.7}
\]

where \( \eta \) is the degree of ionisation and \( m \) is the mass of the ablated particles. The internal energy depends on the temperature and the degree of ionisation. This latter quantity can be calculated using the Saha-Eggert equation, which assumes that the plasma is in Local Thermal Equilibrium (LTE).

For nanosecond ablation pulses at the fluence values used in this study, absorption of laser light by the ablation plume is a very significant process, indeed laser plume interaction is often the effect responsible for formation of the ablation plasma. The two main absorption mechanisms in a monoatomic ablation plume are multi-photon ionisation (MPI) and electron-ion inverse Bremsstrahlung (IBE). Electron-neutral inverse Bremsstrahlung is considered to play a minor role under these experimental conditions.\(^5,23\) The absorption coefficients of the two monoatomic processes are given in equations (3.8) and (3.9) for IBE and MPI, respectively:

\[
\alpha = 1.97 \times 10^{-26} \left( \frac{Z^2 \eta^2 \lambda^3}{T_e^{3.2}} \right) \tag{3.8}
\]

\[
\alpha_{\text{IBE}} = 4.2 \times 10^{-27} \left( \frac{Z^2 \eta^2 \lambda^3}{T_e^{3.2}} \right) \tag{3.9}
\]
\[ \alpha = \sum_k A_k n_k I^b \]  

(3.9)

where \( Z \) is the average ionic state, \( n_i \) is the concentration of the ions, \( \lambda \) is the wavelength of the laser radiation, \( T_e \) is the electron temperature, \( A_k \) is the absorption cross section for a given electronic state \( k \), \( n_k \) is the concentration of the species in the electronic state \( (k) \) to be excited, \( I \) is the intensity of the laser and \( b \) is the number of photons necessary to ionise the atom/ion. The summation ranges over all the electronic states of the atom or ion to be ionised.

Both of the mechanisms are wavelength dependent. The probability of IBE scales with the wavelength, while MPI scales with the inverse of the wavelength. Thus the importance of IBE increases at longer wavelengths while that of MPI declines. At the wavelengths (193 and 248 nm) used in the present work, MPI is the more important mechanism in ablation plasma formation, although MPI might also serve as a seeding mechanism for IBE. The inverse Bremsstrahlung is highly dependent on the ion (and thus the electron) concentration in the plasma, so its importance can increase during the ablation process.

These absorption processes by the plume not only heat up the plume, but also increase the ionisation fraction and the electron density, thus forming a progressively more dense plasma. At high fluences, the electron velocity distribution that develops from laser plasma heating is no longer described by LTE concepts. Instead of a single Maxwellian distribution, a separate thermal and a hot component with different temperatures can briefly co-exist. This simultaneous existence of hot and thermal electrons in the coronal region of the plasma results in sufficient charge separation to cause strong acceleration of the positive ions in the plasma. The physical mechanisms leading to creation of these fast electrons and ions include resonant absorption of the laser photons and magnetic field effects. In the case of pico/femtosecond laser ablation, the laser-plume interaction is non-existent, since most of the plume development occurs after cessation of the laser pulse.

A second approach to describing the plume dynamics follows from theoretical hydrodynamical modelling of the rapid surface vaporisation process associated with the laser ablation process. A rigorous analysis of the process is given in reference 24 and involves the theoretical concept of a Knudsen layer, which defines a collisional regime just in front of the target surface. It has been argued that just 2-3 collisions per emitted
particle suffices for formation of a Knudsen layer. The velocity distribution that results when a Knudsen layer forms is given by:

$$f(v) \equiv \exp \left[ -\frac{2E_i + m(v_x - u_k)^2 + v_y^2 + v_z^2}{2kT_K} \right]$$

(3.10)

where $E_i$ indicates the internal energy of the system, $v_x$, $v_y$ and $v_z$ indicate the velocity in the three spatial coordinates of a mass $m$, $k$ is the Boltzmann constant and $T_K$ is the temperature of the Knudsen layer. The variable $u_k$ is a centre of mass flow velocity in the direction normal to the target surface ($x$-direction). The flow velocity is related to the surface temperature ($T_s$) via:

$$u_k = 1.046 \left( \frac{kT_s}{m} \right)^{1/2}$$

(3.11)

Care has to be taken when using such Centre-of-Mass Maxwell Boltzmann (COM-MB) distributions to fit experimental TOF transients, since equation (3.10) is dependent on the velocity ($v_x, v_y, v_z$) while a TOF transient depends on the position ($x, y, z$) of the detector relative to the source. The transformation of equation (3.10) into a Time of Flight (TOF) situation is performed by introducing the following simplifying conditions:

- The laser spot size and the detector size are small with respect to their spacing
- The detector is an on-axis detector
- The ejection time (= laser pulse duration) is much smaller than the flight time

Let the detector be located at a distance $x$ normal to the target surface and let the flux of the emitted particles in the range $(v_x, dv_x; v_y, dv_y; v_z, dv_z)$ equate $dv_x dv_y dv_z \times v_x f(v)$.

Then if $y$ and $z$ are directions parallel to the target surface and $t$ is the flight time then $dv_z = dy/t$, which is expected for a signal that scales with the detector size ($dy, dz$) and the density (~$1/t$). Since $x$ is parallel to the target normal and the experiment involves TOF we have:
$dv_x = x dt / t^2$ (3.12)

Such is to be expected for a signal that scales as the amount of material into the detector during a temporal window ($\sim x dt / t$) and with the density ($\sim 1/t$). For a flux sensitive detector such as a Faraday Cup, the signal equates:

$$signal \approx Ax^2 t^{-5} \exp \left[ -\frac{m}{2kT} \frac{x}{t} (\frac{x}{t} - u)^2 \right]$$ (3.13)

For a density sensitive detector (for example, a mass spectrometer where ions are formed by electron bombardment in the ionisation region) this equation has to be divided by $v$ to yield a $t^4$ dependence in the pre-exponential factor.

This velocity distribution will be used in Chapter 4 to fit the velocity distributions obtained for the carbon ion signal arising in the 193 nm ablation of graphite. These ion signals were found to be very well approximated by a COM-MB velocity distribution, though the obtained temperatures for these ion distributions are not related to the surface temperature since the ion distribution is subjected to additional heating as a result of laser-plume interactions.

3.1.3. Material deposition

The aspect of material deposition is discussed in detail in Chapter 1.

3.2. Structure of the deposited materials

3.2.1. Diamond Like Carbon (DLC)

DLC is the generic name for carbon-based materials which have a structure and properties that lie between graphite and diamond (the crystalline structures of which are shown in Figure 3.3). DLC materials generally do not possess any long-range
crystalline order and contain between 0-60 % hydrogen depending on their formation route. The \( sp^3/sp^2 \) carbon fraction in DLC is also highly dependent on the deposition conditions, and their microstructure is often described as an ensemble of diamond nodules surrounded by a non-diamond amorphous carbon network. The quality of the films is often described in terms of this \( sp^3 \) to \( sp^2 \) ratio. The structure of any DLC film is inherently metastable; annealing at high temperatures or with high-energy photons/particles will transform its structure into graphitic carbon.

![Graphite and Diamond](image)

**Figure 3.3:** Structure of (a) graphite and (b) diamond.

Since it is possible to adjust the \( sp^3 \) to \( sp^2 \) content of DLC films by changing the growth conditions, it is possible to tune the optical band gap of the material to a chosen value. Some of these films also show excellent electron emission properties, as a result of their very low or even negative electron affinity (NEA) (i.e. the conduction band is above the vacuum level). This means that the electron emission from the surface occurs readily at relatively low applied potential. This property makes it a candidate for future Field Emission devices (FED’s).

### 3.2.2. ZnO

ZnO has a tetrahedral coordination; the most common crystal structure at ambient atmosphere and room temperature is the wurtzite structure, shown in Figure 3.4. Another stable crystal structure at ambient conditions is the zinc blende structure, although the lattice energy is slightly higher for this crystal structure. A third possible crystal structure, which is stable at higher pressures, is the rocksalt structure.
Figure 3.4: (a) Ball and stick image of the wurtzite structure of ZnO, the small balls depict the oxygen atoms, while the larger balls depict the Zn atoms. (b) Picture explaining the stacking sequence along the c-axis, the capital letters stand for Zn atoms.

The experimentally derived values for the $a$ and the $c$ unit cell distances are 3.243 and 5.195 Å, respectively. An important feature of ZnO films deposited by laser ablation methods is that the preferred lattice growth surface is the (002) surface. This is the orientation shown in Figure 3.4, in which the (002) surface is perpendicular to the $c$-axis. This gives an AbBaAb stacking sequence where capital letters stand for Zn for example and the letter coding is given in Figure 3.4(b). The bulk interplanar distances $a$ and $b$ in Figure 3.4(b) are equal to 0.61 and 1.99 Å.

Zinc oxide is a semi-conductor with a band gap of ~3.4 eV, and a tendency to have a metal excess (i.e. $\text{Zn}_{1+x}\text{O}$), which causes it to be an n-type semiconductor. The excess could be due either to zinc interstitials or to oxygen vacancies.\textsuperscript{26}

3.3. Ab initio Theory

3.3.1. The Schrodinger equation and the Born-Oppenheimer approximation

In quantum mechanics, the properties of a system are solely dependent on the wavefunction of the system.\textsuperscript{27} The wavefunction is a time and coordinate dependent function, as given in equation (3.14):
Chapter 3: General Theory

\[ \Psi(x, y, z, t) = \Psi(x, y, z) \cdot \exp \left[ -\frac{iEt}{\hbar} \right] \quad (3.14) \]

The time dependent part of the wavefunction, the exponential factor, is not dependent on any of the spatial coordinates, while the pre-exponential, spatial coordinate dependent, factor is time independent. Since the two factors in (3.14) are mutually independent it is possible to split the wavefunction into a time-dependent and a time-independent part. Since most of the \textit{ab initio} theory involves calculation of stationary, time independent, properties we only consider treatments of the time independent wavefunction in this section. The wavefunction is an abstract concept although the square of the modulus of the wavefunction (or, the product of the wavefunction and its complex conjugate) yields the probability that a particle described by the wavefunction is at a certain position in space, thus:

\[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(x, y, z)|^2 \, dx \, dy \, dz = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi \Psi^* \, dx \, dy \, dz = 1 \quad (3.15) \]

which is a statement of the condition that the wavefunction \( \Psi \) is normalised.

As already stated, all the properties of a quantum mechanical system can be calculated from its wavefunction. The most important property of a system is the energy, which can be calculated from the wavefunction using the (time independent) Schrödinger equation (3.16):

\[ \hat{H} \Psi(x, y, z) = E \Psi(x, y, z) \quad (3.16) \]

where \( E \) stands for the energy of a system described by \( \Psi(x, y, z) \) and \( \hat{H} \) is the Hamiltonian operator. As can be observed from equation (3.16), solving the Schrödinger equation is in fact an eigenvalue problem, where \( \Psi(x, y, z) \) is the eigenfunction of the Hamiltonian operator yielding an eigenvalue \( E \), which is the energy of the system described by \( \Psi(x, y, z) \). In fact, any (physical) observable can be represented by an operator of which \( \Psi(x, y, z) \) is an eigenfunction and the eigenvalues of the operator are the allowed values of the observable. The non-relativistic Hamiltonian operator can be written in terms of \( T_N \) (the nuclear kinetic energy
operator), \( T_e \) (the electronic kinetic energy operator) and \( V \) (the electrostatic potential energy).

\[
\hat{H} = \hat{T}_n(R) + \hat{T}_e(r) + \hat{V}(r, R)
\]  

(3.17)

where \( R \) represents the coordinates of the nuclei and \( r \) the coordinates of the electrons. The potential energy term in equation (3.17) contains the following components:

\[
\hat{V}(r, R) = \hat{V}_{nn}(r, R) + \hat{V}_{en}(r, R) + \hat{V}_{ee}(r, R)
\]  

(3.18)

Reflecting, respectively, nuclear-nuclear interactions, electron-nuclear attractions and electron-electron repulsions. The kinetic energy terms in the Hamiltonian (equation (3.17)) can be separated into a term that depends on the electronic coordinates and a term dependent on the nuclear coordinates. The potential energy terms can also be divided into electronic and nuclear dependent parts by making the following approximation: The electrostatic forces felt by the nuclei and the electrons are of similar sizes. Since the nuclei are much heavier than the electrons, the electronic and nuclear motions can be decoupled by assuming that the motion of the electrons can be treated as if the positions of the nuclei are fixed. This approximation is known as the Born-Oppenheimer approximation. Given this assumption, the total wavefunction can be defined using the Born-Oppenheimer product function:

\[
\psi_{r, R} = \varphi_{e}(r)[R]\chi_{n}(R)
\]  

(3.19)

where \( r \) stands for the electronic coordinates and \( R \) stands for the nuclear coordinates. The coordinates in round brackets stand for a variable of the system, while the coordinates in square brackets stands for a parameter of the system. In the same way the potential energy of the system given in equation (3.18) partitions as follows:

\[
\hat{V}(r, R) = \hat{V}_{nn}(r)[R] + \hat{V}_{en}(r)[R] + \hat{V}_{ee}(r)[R]
\]  

(3.20)
and can be split into a nuclear and an electronic part. If we neglect the kinetic energy of the nuclei we obtain the electrostatic Hamiltonian, which can be used to solve the electronic wavefunctions at a fixed value of internuclear separation \( R \).

\[
\hat{H}_{el} \psi(r, R) = \left[ \hat{T}_e(r) + V(r, R) \right] \psi(r, R) = E_{el}(R) \psi(r, R)
\]  

(3.21)

Since electrons are fermions, the wavefunction has to obey the Pauli Principle, which states that the wavefunction has to be anti-symmetric to the exchange of two electrons, or:

\[
\psi(r_1, r_2, \ldots) = -\psi(r_2, r_1, \ldots)
\]  

(3.22)

This also ensures that two electrons, provided they have the same spin, cannot be in exactly the same position:

\[
\psi(r_1, r_1, \ldots) = -\psi(r_1, r_1, \ldots) = 0
\]  

(3.23)

To ensure anti-symmetry, the wavefunction for \( N \) electrons can be written as a Slater determinant:

\[
\psi(1, 2, \ldots, N) = \left( \frac{1}{N!} \right)^{1/2} \begin{vmatrix} \phi_s(1) & \phi_s(1) & \cdots & \phi_s(1) \\ \phi_s(2) & \phi_s(2) & \phi_s(2) & \phi_s(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_s(N) & \phi_s(N) & \phi_s(N) & \phi_s(N) \end{vmatrix}
\]  

(3.24)

where \( \phi \) is the spin orbital for each electron (the spin orbital contains the spatial and the spin variables). The electron spin is a purely quantum mechanical property (it has no equivalent in classical mechanics) and can take two different values \(+\frac{1}{2}\) and \(-\frac{1}{2}\) (often referred to as spin 'up' and spin 'down').

Exact solution of the electronic Schrödinger equation is impossible, except for simple one-electron systems like \( H \), \( He^+ \) and \( H_2^+ \). This is the same as stating that the wavefunction and the spin orbitals defined by equation (3.24) are only known exactly.
for these one-electron systems. For bigger systems the wavefunction has to be approximated in the following way:

\[
\phi_i = \sum_m c_{i,m} \gamma_m
\]  

(3.25)

where \( \gamma_m \) represents atomic orbitals and \( c_{i,m} \) is the contribution each atomic orbital makes to a specific molecular orbital (MO). The wavefunction is thus represented by a Linear Combination of Atomic Orbitals (LCAO). The atomic orbitals for these stems are approximated by 'hydrogen-like' orbitals (i.e. s, p, d etc. orbitals), which have the same angular behaviour as hydrogen orbitals but have an atom dependent radial behaviour. These orbitals are commonly called Slater orbitals. The Slater s-orbitals are difficult to treat computationally (they exhibit a cusp at the origin) and are thus commonly replaced by a combination of Gaussian basis functions (primitives). The assembly of basis functions for a specific atom is called a basis set.

Since the wavefunction for multi-electron systems is not the exact wavefunction of the system, solving the Schrödinger equation for such systems yields an eigenvalue which is similarly an approximation of the exact energy. It can be shown that the eigenvalues obtained with an approximate wavefunction will always be higher than the ground state energy calculated with the true wavefunction. This is expressed mathematically by equation (3.26) for a normalised wavefunction, and is called the variational theorem:

\[
E = \int_{-\infty}^{\infty} \psi^* H \psi \, dv \geq E_0
\]  

(3.26)

A consequence of the variational theorem is that the energy calculated with basis sets which are increasingly better approximations of the real wavefunction will yield increasingly lower energies.

During the development of quantum mechanics a large number of schemes were constructed to solve the Schrödinger equation numerically. These methods are called \textit{ab initio} methods. Such calculations treat a molecule as a collection of positive nuclei and negative electrons that are subjected to Coulombic interactions.
In this study two different types of *ab initio* calculation were performed, namely Hartree-Fock (HF) and Density Functional Theory (DFT) calculations. Both techniques are discussed in more detail in the following sections.

### 3.3.2. HF Theory

In HF theory, the Schrödinger equation is solved numerically by the introduction of Self Consistent Fields (SCF). The assumption behind the technique is that any electron moves in a potential which is a spherical average of the potential due to all the other electrons. The Schrödinger equation is calculated for this specific electron in this specific electric field. Since the wavefunction, and subsequently the molecular orbitals for each electron, is not known in advance the final solution of a SCF problem is reached iteratively. First, an initial guess for the wavefunction is provided. With this initial guess, the Schrödinger equation for the individual electrons is solved. The wavefunction so obtained will give an improved averaged potential experienced by the individual electrons, which is used to refine the solution of the Schrödinger equation. This iteration cycle is repeated until the energy change for the system drops beneath a given threshold. This gives a set of self-consistent orbitals.

The Restricted HF theory approximates the structure of a (open or closed shell) molecule as a single Slater determinant (equation (3.24)). The Hamiltonian for this system has the following form:

\[
\hat{H} = \sum_i \hat{H}_i + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{i,j}}
\]

(3.27)

where \( \hat{H}_i \) is the 'hydrogen-like' Hamiltonian for electron \( i \) in the field of the bare nuclei and the second term in the equation stands for the electron-electron repulsion (in atomic units). The factor \( 1/2 \) in the electron-electron repulsion is there to avoid double-counting of the interactions in the double sum.

The Hartree-Fock equation for a space orbital \( \psi_s \) occupied by electron \( i \) in the determinant is:
\[ H_I + \sum_r (2J_r - K_r) \psi_s(i) = \epsilon_i \psi_s(i) \] (3.28)

where \( J_r \) (Coulomb operator) and \( K_r \) (Exchange operator) are defined as follows:

\[
J_r \psi_s(i) = \left\{ \int \psi_s^*(j) \frac{1}{r_{ij}} \psi_s(j) \, d\tau_j \right\} \cdot \psi_s(i)
\] (3.29)

\[
K_r \psi_s(i) = \left\{ \int \psi_s^*(j) \frac{1}{r_{ij}} \psi_s(j) \, d\tau_j \right\} \cdot \psi_s(i)
\] (3.30)

The Coulomb operator takes into account the Coulombic potential energy of electron \( i \) when its spatial position is given by \( \psi_s(i) \) and when it is interacting with an electron in the space orbital \( \psi_s \). The exchange term is a quantum mechanical correction term that allows for the effects of spin correlation. The sum on the left of equation (3.28) runs over all occupied space orbitals, and the value \( \epsilon_i \) is called the one electron orbital energy. The one electron orbital energies of the system can be calculated by multiplying both sides of equation (3.28) by \( \psi_s^* \) and then integrating over all space. The total electronic energy of the molecule is then calculated as:

\[
E = 2 \sum_i \epsilon_i - \sum_r \sum_s (2J_{rs} - K_{rs})
\] (3.31)

where \( J_{rs} \) and \( K_{rs} \) are the Coulomb and the exchange integrals, respectively.

HF theory provides a first approximation to the wavefunction. Although the theory treats the Pauli exclusion principle correctly, by not allowing two electrons to occupy the same spin orbital, and includes electron-electron repulsion effects in an averaged way, it does not include any direct electron interaction between two electrons of opposite spin. The energy corresponding to this interaction is the energy difference between the true energy of the system and the HF limit and is called the correlation energy. In the following section we discuss a technique that allows calculation of (part of) the correlation energy, namely DFT theory.
3.3.3. DFT Theory

DFT theory adopts a different approach to solving the Schrödinger equation. The basis of the theory is the proof by Hohenberg and Kohn that the ground-state electronic energy is determined completely by the electron density $\rho$. The importance of this proof is that the complexity of the wave function will increase upon increasing the number of electrons (the wavefunction is dependent on the coordinates of all the electrons), while the complexity of the electron density is independent on the number of electrons. The main problem of the technique is that each different density yields a different ground-state energy and the functional connecting the energy with the electron density is not known.

As with the HF approach the electronic energy functional may be divided into three parts, the kinetic energy $T[\rho]$, electron-nuclear attraction $V_{ne}[\rho]$ and electron-electron repulsion $V_{ee}[\rho]$. The electron-electron repulsion can be divided into the Coulomb ($J[\rho]$) and Exchange ($K[\rho]$) parts and implicitly includes electron correlation in all terms (as opposed to HF theory). The $V_{ne}[\rho]$ and the $J[\rho]$ terms are given by their classical expressions.

$$V_{ne}[\rho] = \sum_i \int \frac{Z_i \rho(r)}{|R_i - r|} \, dr$$

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

Early attempts at deriving functionals for the kinetic and the exchange energy were based on the solution of the problem of a non-interacting uniform electron gas, but this assumption does not hold for atomic and molecular systems, since it fails to predict any bonding between atoms.

The foundations for using DFT in computational chemistry stem from introduction of orbitals by Kohn and Sham. The basic idea of the Kohn-Sham (KS) formalism is to split the kinetic energy functional into two parts, one which can be calculated exactly, the other a small correction term.

Assume a Hamiltonian operator with the following functional form ($0 \leq \lambda \leq 1$):
\[
\hat{H}_\lambda = \hat{T} + \hat{V}_{\text{ext}}(\lambda) + \lambda \hat{V}_{\text{ee}}
\]  

(3.34)

The \(\hat{V}_{\text{ext}}\) operator is equal to \(\hat{V}_{\text{ne}}\) for \(\lambda = 1\). For intermediate \(\lambda\) values, however, the external potential \(\hat{V}_{\text{ext}}\) is adjusted so that the same density is obtained for both \(\lambda = 1\), the real system, and \(\lambda = 0\), a hypothetical system with non-interacting electrons. For the \(\lambda = 0\) case the exact solution to the Schrödinger equation is given as a Slater determinant composed of MO's, \(\phi_i\), for which the exact kinetic energy is given by:

\[
T_S = \sum_{i=1}^{N} \left\langle \phi_i \left| -\frac{1}{2} \nabla^2 \right| \phi_i \right\rangle
\]

(3.35)

The subscript in \(T_S\) denotes that the kinetic energy is calculated from a Slater determinant. The kinetic energy in equation (3.35) corresponds to the kinetic energy for a system with non-interacting electrons, and therefore equation (3.35) is only an approximation to the real kinetic energy, although the difference between the exact kinetic energy and the kinetic energy calculated with non-interacting orbitals is small.

A general expression for the total electronic energy calculated by DFT can be given as:

\[
E_{\text{DFT}}[\rho] = T_S[\rho] + E_{\text{xc}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]
\]

(3.36)

and, by equating \(E_{\text{DFT}}\) to the exact energy an expression of the exchange-correlation term can be obtained and thus defined as:

\[
E_{\text{xc}}[\rho] = (T[\rho] - T_S[\rho]) + (E_{\text{ee}}[\rho] - J[\rho])
\]

(3.37)

The first term in parenthesis can be considered as the kinetic correlation energy while the second term contains both the exchange and correlation potential energy.

Computationally, the DFT method thus provides a higher level of theory (since correlation energy is taken into account) at a similar computational cost to that of the HF theory. The major problem with implementing DFT methods is the derivation of suitable formulas for the exchange-correlation term. Assuming that an exact functional is available, the problem reduces to solving the determinant of a set of orthogonal
orbitals which minimise the energy via an SCF iterative method. The problem can be expressed as the Kohn-Sham equation, which is similar to the Hartree-Fock equation (equation (3.28)).

\[ \hat{H}_{\text{KS}} \phi_i = \varepsilon_i \phi_i \]  \hspace{1cm} (3.38)

The Kohn-Sham Hamiltonian can be split into different terms:

\[ \hat{H}_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_{\text{ne}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r})}{|\mathbf{r}_i - \mathbf{r}_f|} \mathbf{\hat{r}}_j + V_{\text{xc}}(\mathbf{r}_i) \underbrace{V_{\text{eff}}}_{\mathbf{V}} \]  \hspace{1cm} (3.39)

Solution of the Kohn-Sham equation is computationally very similar to solving the HF equation. The numerical methods used for HF theory can also be used for DFT theory and analogously, the KS orbitals can be expanded in a set of basis functions. The advantage of DFT over HF calculations is that the former includes at least an approximation to the correlation energy.

During the development of DFT methods various different functional forms for the exchange-correlation potential have been proposed, spanning a number of different DFT methods. These functional forms are designed to have a limiting behaviour (the uniform electron gas limit) and are determined by fitting parameters to known accurate data. Three different methods have been developed to date; Local Density methods, Gradient Corrected Methods and Hybrid methods.

The Local (Spin) Density Approximation (L(S)DA) assumes that the density is a slowly varying function which can be locally treated as a uniform electron gas. The correlation energy of a uniform electron gas has been determined by Monte Carlo methods for a number of different densities. The results are interpolated using a suitable analytic expression, called the Vosko, Wilk and Nusair (VWN) formula. The L(S)DA approximation generally underestimates the exchange energy by \(\sim 10\%\), thereby creating errors which are larger than the whole correlation energy. Electron correlation is overestimated by a factor of \(\sim 2\) and, as a consequence, bond strengths are overestimated. Thus notwithstanding the specific inclusion of electron correlation, L(S)DA provides results that are only of a similar accuracy to the HF results.
Improvements to the L(S)DA approach are based on consideration of a non-uniform electron gas. This can be achieved, in part, by making the exchange and the correlation energy depend not only on the density, but also on the derivatives of the density. These so-called Gradient Corrected methods involve different expressions for the exchange energy term ($E_x$) and the correlation energy term ($E_c$). Many different functionals have been proposed, each with a specific dependency on the density and its derivatives.

From the Hamiltonian in equation (3.34) and the definition of the exchange energy in (3.37), it is possible to make an exact connection between the exchange-correlation energy and the corresponding potential connecting the non-interacting reference and the actual system. The resulting equation, the Adiabatic Connection Formula (ACF), involves an integration over the parameter $\lambda$ which "switches on" the electron-electron interaction.

$$E_{xc} = \int_0^1 \langle \psi_\lambda | V_{xc}(\lambda) | \psi_\lambda \rangle d\lambda$$

In the crudest approximation the integral is given as the average of the two end points.

$$E_{xc} = \frac{1}{2} \left\langle \psi_0 | V_{xc}(0) | \psi_0 \right\rangle + \frac{1}{2} \left\langle \psi_1 | V_{xc}(1) | \psi_1 \right\rangle$$

In the $\lambda = 0$ limit, the electrons are non-interacting and there is consequently no correlation energy. In this case the exchange energy is exactly that given by HF theory. The last term in equation (3.41) is still not exactly known, but the exchange energy can be approximated by a suitable combination of L(S)DA, exact exchange and a gradient correction term while the correlation energy can similarly be taken as the L(S)DA formula plus a gradient correction term. The best known hybrid method is the Becke 3 parameter functional and is described by equation (3.42),

$$E_{xc}^{B3} = (1-a)E_x^{LS} + aE_x^{exact} + b\Delta E_x^{B88} + E_c^{LS} + c\Delta E_c^{GXC}$$

Where B88 is an exchange functional. The Becke 3 functional hybrid corrected methods typically show the best performance. Gradient Corrected correlation
functionals suitable for use in this hybrid method include the Lee-Yang-Parr (LYP),
the Perdew 86 (P86) or the Perdew-Wang 91 (PW91) functionals. The present study
employs the Becke 3 parameter functional method together with the LYP
correlation functional.

3.3.4. Properties calculated from the wavefunction

As mentioned earlier the wavefunction of a system determines all the properties of
that system. The most important property is the energy of the system and the
calculation of the total energy via HF or DFT is discussed in the former paragraphs.

Another important property that can be calculated is the charge distribution in the
computed system. This charge distribution determines the bonding behaviour in
molecules, and analysis of the charge distribution allows prediction of whether a
specific bond is best approximated as covalent or ionic. The charge distribution can be
plotted as a charge density plot, or alternatively, a mathematical analysis can be
performed, to obtain a more localised picture of the charge distribution. In these charge
redistribution schemes, a part of the total electron density is attributed to the atoms
contained within the molecule thereby giving a more intuitive picture of the charge
localisation. The most widely used scheme for charge redistribution is the Mulliken
population analysis.

To illustrate the approach, let us consider the example of a diatomic molecule with
one (normalised) atomic orbital on each nucleus, i.e.:

\[ \varphi = c_A \phi_A + c_B \phi_B \] (3.43)

If we square the modulus of the wavefunction, integrate and multiply by the number of
electrons (N) in the MO, we obtain:

\[ N = Nc_A^2 + 2Nc_Ac_B S_{AB} + Nc_B^2 \] (3.44)

where:
Chapter 3: General Theory

\[ S_{AB} = \int \phi_a \phi_b \, d\nu \quad (3.45) \]

In the Mulliken population analysis the terms \( Nc_A^2 \) and \( Nc_B^2 \) are referred to as the net electron densities on atoms A and B, respectively, and the cross term \( 2Nc_A c_B N_{AB} \) is referred to as the overlap population or the bond order. If we assume that the cross-term can be divided equally between atoms A and B, the a gross electron population on each atomic centre can be defined:

\[ N(A) = N \left( c_A^2 + c_A c_B S_{AB} \right) \quad (3.46) \]

\[ N(B) = N \left( c_B^2 + c_A c_B S_{AB} \right) \quad (3.47) \]

and the gross charge can be defined as the sum of the nuclear and the electronic charge on the atoms. Generalisation of these concepts to extended basis sets and polyatomic molecules is straightforward. It is obvious that this definition contains several arbitrary assumptions. For example, it is highly dependent on the basis set used to describe the system, and the allocation of the overlap distribution to the atoms is arbitrary. Nevertheless, this approach can provide very useful insights into the charge distribution. Taking into account the aforementioned restrictions.

3.3.5. Plane Wave Approximation

The system studied theoretically in this thesis (zinc oxide) is a crystalline solid. The approach to calculating the electronic structure and properties of solids is summarised in the Bloch theorem. This assumes that the wavefunctions of the electrons in a crystal have the Bloch form:\[ \psi_A(r) = e^{ikr} u_A(r) \quad (3.48) \]
where \( u_k(r) \) is a function that has the lattice periodicity, i.e. \( u_k(r) = u_k(r + t_m) \) where \( t_m \) is any relative lattice translation. The Bloch function, \( \Psi_k \) consists of a free electron wavefunction \( e^{ikr} \), modulated by the \( u_k \) function that has the periodicity of the lattice. Thus it is a modulated plane wave. It can be readily proven that the wavefunction must be of the form

\[
\psi(x + a) = \psi(x) e^{2\pi i m / a^3}
\]

which is the Bloch condition on the wavefunction. In this way the Bloch theorem ensures that the periodicity of the crystal structure is reflected in the periodicity of the electronic structure. This theorem also enables calculation of the electronic structure of a crystal lattice by calculating the wavefunction of the appropriate unit cell. The assumption that the electronic wavefunction is a plane wave in the three dimensions readily extends this solution to the whole crystal lattice. Surfaces can be studied also, by assuming electronic periodicity in only two dimensions, while the electronic structure in the third dimension is calculated independently.

### 3.3.6. Polar surfaces in solids

Polar surfaces of compound materials are of prominent interest. The orientation of the surface is such that each repeating unit perpendicular to the surface bears a non-zero dipole moment. The resulting macroscopic dipole moment induces an electrostatic instability, which can only be cancelled by the introduction of compensating charges in the outer planes. The various ways by which the lattice can electronically relax are discussed below.\(^{38}\)

The importance of polar surfaces to the present work follows from the observation that the dominant growth surface of ZnO, the (002) surface, is a polar oxide surface. To understand the implications of this observation we have performed \textit{ab initio} calculations to assess the electronic structure of this surface. The results are discussed in Chapter 5.
Chapter 3: General Theory

3.3.6.1. Criterion for surface polarity

According to classical electrostatic criteria, the stability of a surface depends on the characteristics of the charge distribution of the repeating structural unit in the direction perpendicular to the surface. Three different cases can be distinguished and are shown in Figure 3.5. Type 1 and 2 surfaces have a dipole moment in their repeat unit and are thus potentially stable. In contrast, type 3 surfaces have a diverging electrostatic surface energy, not only because of the dipole moment on the surface, but also on all of the repeating units throughout the material.

![Figure 3.5: Classification of different surfaces.](image)

Figure 3.5: Classification of different surfaces. [ Indicates the extent of the repeat unit and circles with different colours represent the different ions in the lattice. Type 1 and type 2 are stable surfaces, the difference between the two being that surface 2 has a non-zero charge separation along the axis normal to the surface (Q ≠ 0). Type 3 surfaces are inherently unstable since they also exhibit a dipole moment along the axis normal to the surface.

A simple representation of the electrostatic field and potential generated by a Type 3 surface along the polar direction is given in Figure 3.6. Two layers with opposite charge ±σ alternate along the surface normal, with interlayer spacing \( R_1 \) and \( R_2 \). The total dipole moment (\( M = NσR_1 \)) is obviously proportional to the slab thickness in (a), which, in the limiting case of an infinite number of layers, makes the surface energy divergent. To stabilise the surface, the charge density of the most outer layers can be modified so as to cancel out the macroscopic component of the dipole moment and thereby cancel the polarity. This can be achieved by assigning a value given by equation (3.50) to the charge density on the outer layers of the slab, as shown in Figure 3.6(b).
\[ \sigma' = \frac{\sigma R_2}{(R_1 + R_2)} \] \hspace{1cm} (3.50)

This results in a total dipole moment \( M = \sigma R_1 R_2 / (R_1 + R_2) \), which is no longer proportional to the slab thickness.

Figure 3.6: Spatial variation of the electrostatic field and potential generated along the polar direction in a type 3 surface, (a) without surface relaxation (yielding surface energy = \( \infty \)) and (b) with surface relaxation (yielding a finite value for the surface energy).

A polar surface can thus be stabilised by a charge compensation in the outer layers. This implies that either the charges or the stoichiometry in the surface layers needs to be modified in comparison with their bulk values to achieve polar surface stabilisation. The different scenarios to cancel the polarity are thus:

- Stoichiometry changes in one or several surface layers. This can lead to phenomena like reconstruction and terracing, depending on the order within the vacancies or adatoms.
- Inclusion of foreign atoms or ions, coming from the residual atmosphere in the experimental set-up, to provide the necessary charge compensation.
Charge compensation may result from an electron redistribution in response to the polar electrostatic field. This can be studied in some detail by \textit{ab initio} calculations.

Which relaxation mechanism will be the most favourable is dictated by energetic considerations. There will always be enough electronic degrees of freedom to relax the material via the third of the above mechanism, but, in most cases, one of the other two mechanisms will actually provide a route to a lower surface energy.

3.3.6.2. \textit{Relevant processes for cancelling the polarity}

The mechanisms that govern electron redistribution within the lattice, and thus the polarity of the lattice, are now discussed in more detail.

One process that can be considered is surface relaxation. As Figure 3.6 shows, surface relaxation will not cancel the polarity if the relaxation is not accompanied by a change in the surface layer charge densities, since the dipole moment is determined by the charges and layer spacings in the bulk unit. Furthermore surface relaxation will only stabilise an electrostatically stable surface.

Similarly, change in covalency in the surface layers will not contribute much to the stabilisation of these polar surfaces. Again Figure 3.6 readily shows that reduction of the charge on the two top layers, because of an increase in covalency, will not cancel the polarity.

Charge compensation on stoichiometric surfaces can only be achieved by a formal charge transfer from one surface to the other surface, thereby creating an 'induced dipole moment' which counteracts the original dipole moment. This is achieved by partially filling the conduction band surface states or by depleting the valence band surface states.

The second way the lattice can relax is via a change of the surface stoichiometry. For example, to remove the charge necessary to counteract the dipole moment on a ZnO (001) surface can be calculated with equation (3.50) and is \( \frac{1}{4} \) of the total charge density \( (R_I=0.61 \text{ and } R_\perp=1.99 \text{ Å}) \). So, to counteract the bulk dipole moment, \( \frac{1}{4} \) of the cations and anions in the ZnO surface layer have to be removed.
3.3.6.3. Former studies on ZnO

The (001) Zn terminated and (00\overline{1}) O terminated surfaces of ZnO have been studied by grazing incidence X-Ray diffraction (GIXD). In this study the Zn terminated surface shows a +0.05 Å outward relaxation associated with a 0.75 occupancy of the Zn sites in the outer layer. The O terminated surface is relaxed inward by -0.03 Å, and the occupancies of both the outer and the underlying layers are different from their bulk value. This picture illustrates that a ZnO polar surface relaxes preferentially by changing the surface stoichiometry rather than via charge redistribution.

Theoretical LSDA calculations on embedded clusters have shown that spontaneous charge redistribution takes place on stoichiometric terminations, as expected from the electrostatic criterion. This has been attributed to a change in covalent bonding character on the Zn face, and a partial filling of the surface states on the oxygen face. In a very recent study, the polar (001) and (00\overline{1}) surfaces have been geometry optimised to yield an energy minimum with relatively small relaxations. The calculations indicate that the surfaces are stabilised by a charge transfer between the two surfaces of 0.17 e, which leads to metallic surface states.

3.4. References

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4. The UV pulsed laser ablation of graphite and the pulsed laser deposition of Diamond Like Carbon

The pulsed laser ablation (PLA) and deposition of graphite have been studied in this work by various techniques. The ablation event has been studied using an assembly that allows direct investigation of the absorption of the graphite plume by monitoring the amount of laser light transmitted through a small hole (200 µm diameter), mechanically drilled in the target surface, as a function of fluence. This direct observation of the laser light yields a qualitative understanding of extent to which and the processes by which, laser light is absorbed by the ablation plume.

Further investigations of the laser induced ablation plume have been performed using wavelength, time and spatially resolved OES and by temporal and angular resolved Faraday Cup measurements of the positively charged ions. The optical emission studies give information about the excited and radiatively decaying species within the plume while the Faraday Cup measurements provide information about the total ion distribution. Comparison of these results has led to the formulation of a simplified 2-dimensional model of the ablation event to explain the apparent contradictions between the optical emission and the Faraday Cup results.

In addition, the pulsed laser deposition of Diamond Like Carbon (DLC) has been studied from ablation of two different targets, namely graphite and CVD diamond. The sp³ fractions of the deposited films were derived from Raman spectrometry, and their Field Emission were studied. Finally, as a small addition to this work, doping of DLC films with sulphur has been attempted, and the deposition process and the produced films have been partially characterised.

4.1. Introduction

Graphite is an attractive target material for fundamental studies of PLA, both because of its intrinsic elemental simplicity and because of the wide potential...
applicability of hard hydrogen-free diamond-like carbon (DLC) films.\textsuperscript{1} It has been the subject of several previous investigations; indeed, graphite was one of the first target materials to be ablated when the pulsed ruby laser first became available.\textsuperscript{2} Subsequent studies of the PLA of graphite using long excitation wavelengths (e.g. 1064 nm) have shown the ablation plume contains a high proportion of small carbon cluster species (ions and neutrals).\textsuperscript{3-5} DLC films in which an estimated 70\% of the C atoms show sp\textsuperscript{3} (tetrahedral) co-ordination have been reported following 1064 nm laser ablation of graphite, in vacuum, but only at laser intensities approaching 10\textsuperscript{10} W/cm\textsuperscript{2}.\textsuperscript{6} Such observations should be contrasted with PLA induced using short wavelength ultraviolet (UV) laser radiation (e.g. 193 nm radiation), where the plume is dominated by atomic species (C neutrals and ions),\textsuperscript{7-9} and high quality DLC films containing >90\% sp\textsuperscript{3} bonded C atoms have been reported using much lower intensities (\textasciitilde5 \times 10\textsuperscript{8} W/cm\textsuperscript{2}).\textsuperscript{6,10-13} Such observations support the consensus view that high (~100 eV) impact energies encourage formation of dense sp\textsuperscript{3} (rather than graphitic) networks in the deposited film,\textsuperscript{1,14-19} and that high ejection velocities are a feature of UV laser ablation rather than more thermally driven (VIS-IR) ablation. Nonetheless, many details of the ablation process including, for example, factors which affect the plume composition and properties, and how these then in turn influence the resulting film characteristics, merit further study.

4.2. Experimental

The general experimental set-up has been discussed in detail in Chapter 2. The experiments performed on the pulsed laser ablation of graphite were: direct measurement of the attenuation of the laser light by the plume, and optical emission and the Faraday Cup measurements of particles within the plume. The angular dependency of the total ion signal was determined via Faraday Cup measurements in combination with the translation stage target holder. This target holder can be rotated manually about the vertical axis (z) and locked in any user-selected orientation relative to the laser propagation axis. The translation stage rasters the target in the zy plane relative to the fixed laser focus, thereby allowing each laser shot to ablate a fresh area of the graphite
surface. The optical emission was recorded using the procedures described in Chapter 2, both OES and CCD camera imaging were employed.

The pulsed laser deposition studies employed standard conditions for DLC film growth, i.e. high vacuum, room temperature substrate. The films were analysed by Raman spectroscopy and subjected to Field emission testing.

### 4.3. Direct measurement of the attenuation of the laser light by the plume

Attenuation of the laser light by the plume was studied directly, by recording the temporal transient of the laser pulse obtained by coupling the laser light onto a fast photodiode after it had propagated through a small, mechanically drilled, hole through the target. Pictures of a typical hole are as shown in Figure 4.1(a). The dimensions of the hole were chosen so as to be sufficiently small compared to the laser spot size to cause only a minor perturbation to the amount of ejected particles, but big enough to allow a detectable amount of light through the aperture. Given a laser pulse footprint on the target of $1 \times 0.4 \text{ mm}^2$ and a hole diameter of 200 µm the area of the hole is less than 10% of the total ablated area. An image of the post-ablated area is given in Figure 4.1(b).

![Figure 4.1: Selected SEM images of the mechanically drilled holes in the target, (a) top view, the hole diameter is ~ 200 µm (b) side view after ablation, the hole is positioned in the middle of the ablation spot.](image)

This set-up is used to investigate the absorption mechanism of the laser light by the ablated plume. The two main absorption mechanisms in a monoatomic ablation plume
are multi-photon ionisation (MPI) and electron-ion inverse Bremsstrahlung (IBE). Electron-neutral inverse Bremsstrahlung plays a minor role under these experimental conditions. Another mechanism that could cause attenuation is photodissociation of larger clusters emitted by the surface. To our knowledge, there is no quantitative information about the ejection rate of larger clusters from graphite arising from 193 nm ablation, although the optical emission of the ablation plume (section 4.4) suggests that larger clusters are a minor fraction in the plume.

The IBE and MPI processes were discussed in more detail in Chapter 3. IBE scales with the wavelength while MPI scales with the inverse of the wavelength. Thus at 193 nm MPI is considered to be the more important mechanism for plasma formation, although MPI can also be a seeding mechanism for IBE since the latter is highly dependent on the ion (and inherently the electron) concentration in the plasma.

MPI is still quite improbable in the case of a carbon atom (ionisation potential (IP) = 11.26 eV) with 193 nm photons, since it involves a two photon excitation process. However, this assumption may merit closer scrutiny in the case of both ArF and KrF laser ablation of carbon targets since two low lying metastable excited states of atomic carbon (the 2p², ¹D and 2p², ¹S states) coincidentally have strong one photon absorptions that fall within the respective excimer laser bandwidths. Pappas et al. have highlighted the particularly good resonance between the 2p¹3s¹, ¹P<->2p², ¹D transition at 193.09 nm and the peak of the ArF excimer laser output. Given that the ¹D state of atomic carbon lies at an energy 1.263 eV above that of the ³P ground state, and assuming a typical surface vaporisation temperature \( T_s \sim 4500 \) K in the focal spot on the graphite target, simple thermodynamic considerations would suggest that ~2% of the ablated C atoms will be formed in the metastable excited state. The 2p¹3s¹, ¹P<->2p², ¹D transition must provide strong resonance enhancement to the two photon ionisation of these atoms in the plume; at the prevailing laser intensities this will be a very efficient process and greatly enhance the local electron and ion densities.

Both of the processes could attenuate the temporal lineshape of the incident laser beam in two different ways. The IBE process would be expected to attenuate the trailing edge of the temporal laser profile since it is a cascade mechanism, which would be more prevalent at later timescales. MPI would attenuate the highest intensity region of the temporal laser lineshape thus effectively broadening the lineshape. This is shown in Figure 4.2.
Chapter 4: Laser ablation of graphite

Figure 4.2: Schematic illustration of the different attenuations of the laser pulse profile by MPI and IBE in the plume (LP = laser pulse). MPI will result in an attenuation of the peak intensity, while IBE will tend to attenuate the trailing edge of the laser pulse profile.

The temporal lineshapes of the laser light are given in Figure 4.3. The lineshapes could be easily fitted to a split gaussian and analysed as such to eliminate the experimental noise on the curves. The important figures to compare are FWHM values and the differences in total signal with change of fluence. Important to note is that these are all relative measurements. Measurements of the temporal laser lineshape without a target at higher fluences tended to saturate the detector while pulses at lower fluences (5 J/cm²) yielded a value ~17 ns FWHM. The error bars on the FWHM are also limited by the sample rate of the oscilloscope (2.5 GHz) giving an accuracy of 0.4 ns.
Figure 4.3: Experimentally monitored laser pulse profiles for four different fluences. The black squares represent points of the fitting function used to fit the data recorded with a fluence of 5 J/cm². Zero is not well defined for these transients, the oscilloscope was triggered from the rising edge of the temporal profile.

The results of the attenuation experiment are summarised in Figure 4.4. The relative values of the FWHM (Figure 4.4(a)) do not show large differences, but the total signal shows a well-defined trend with increasing incident pulse energy (Figure 4.4(b)). The FWHM variation suggests that the attenuation process is a convolution of both MPI and IBE, since the two attenuation mechanisms will affect the temporal lineshape in opposite ways. The apparent relative decrease in the FWHM at the highest fluence might indicate a greater importance of IBE at higher fluences although the intrinsic error bars on the measurements (± 0.4 ns) are too high for this to be a quantitative conclusion. The total detected signal levels out at fluences higher than 12 J/cm² indicating an increasing attenuation that could correlate with a cascade mechanism like IBE, in accordance with the figures obtained for the FWHM. Comparing the values of the integrated detected signal for an incident fluence of 20 J/cm² with those for 5 J/cm² indicates that the plasma exhibits an additional absorption of 60% at the highest fluence.
Figure 4.4: (a) The FWHM and (b) the total signal of the recorded laser profiles as a function of the fluence (5-20 J/cm²) of the incident laser light. The origin (0,0) is included in the latter graph as a reference. The error bars are the standard deviations taken from four independent measurements.

The observed behaviour can be rationalised as follows. The laser photons cause the crystal lattice to heat up and emit atoms and ions. The percentage of the total material flux ejected as ions as a result of a thermal evaporation mechanism is insignificant. The main ion generating process in this initial regime will be MPI, given the small initial ionisation fraction, the dependencies of the various possible ion forming processes on the experimental conditions and the fact that the MPI process is resonance enhanced. This, in turn, will lead to an increase in the local absorption due to electron-neutral and, particularly, electron-ion inverse Bremsstrahlung which, having a continuum spectrum, can interact with all photons within the ArF laser bandwidth. Thus the initial resonance enhanced two photon ionisation of metastable C (1D) atoms is considered to act as a localised, and highly non-linear, 'seed' for further absorption and ionisation processes. Quantitatively, the results indicate that plasma absorption of the laser light becomes a prevalent mechanism for plume heating at fluences above 12 J/cm².

These results can be compared and contrasted with recent results for Poly-Methyl Methacrylate (PMMA) and Poly-Imide ablation (Pl). The ablation of polymers is considered to be a much purer photoablation, with direct excitation of chromophoric groups in the lattice, which makes straightforward comparison
impossible. Nevertheless the deduced percentages of the incident laser light absorbed by the plume (45 % at a fluence of 4 J/cm², rising to 80 % at higher fluences (10 J/cm²)) is very comparable to the attenuation levels we deduce for graphite at fluences > 12 J/cm².

4.4. Optical emission of the ablation plume

4.4.1. Wavelength dispersed emission

The ablation plume arising in the 193 nm ablation of graphite in vacuum is clearly visible to the naked eye. When viewed from above, at lower fluences ($F \sim 12.5 \text{ J/cm}^2$), the plume appears as a small volume of intense white plasma localised at the laser focus, and a more extensive diffuse green emission, which appears symmetrically distributed about the surface normal and fills the major part of the forward hemisphere. Occasional thin bright tracks originating from the focal volume with seemingly random trajectories are also evident. These we attribute to incandescent sputtered macroparticles (see also Chapter 6). At higher $F$, these emissions are supplemented by a shaft of purple fluorescence, also originating from the focal volume. This emission appears to be distributed asymmetrically about the surface normal. Indeed, when the long axis of the rectangular laser output is parallel to the viewing axis (i.e. along $z$) the purple shaft appears to follow an axis that approximately bisects the laser propagation axis and the surface normal. These laser fluences fall in the regime characterised by significant absorption of the laser light by the ablated plume as indicated in section 4.3.
Figure 4.5: Wavelength dispersed spectra of the plume emission accompanying 193 nm PLA of graphite in vacuum, using 20 J/cm² laser pulses incident at 45° to the surface normal and with the long axis aligned vertically. Spectra (a)-(d) were recorded at θ ~+22° to the surface normal, at distances d = 3, 7, 12 and 20 mm from the focal region, respectively. (e) is taken at d = 7 mm and θ ~-22° axis. C emission lines are indicated by the comb above (a), ♦ indicates lines appearing in second order, while all other lines are associated with C⁺ or C²⁺ ions as described in the text.

Figure 4.5 shows several low resolution (Δλ = 0.8 nm) wavelength dispersed emission spectra covering the range 225-1025 nm recorded from localised regions of the ablation plume resulting from 193 nm PLA of graphite in vacuum, using 20 J/cm² laser pulses incident at 45° to the surface normal and with the long axis of the laser output aligned vertically. Spectra (a)-(d) were recorded along the shaft of purple emission, i.e. at θ ~+22° to the surface normal (positive θ corresponds to angles on the same side of the surface normal as the laser propagation), viewing at distances d = 3, 7.
12 and 20 mm from the focal region. Contrast spectrum (b) with that shown in (e), which was also recorded at \( d = 7 \) mm but now monitoring along the \( \theta \sim 22^\circ \) axis.

Each such spectrum was obtained by joining three overlapping 300 nm sections recorded using the Instaspec IV system (30 laser shot accumulations). The displayed spectra have not been corrected for the wavelength dependence of the quartz fibre bundle transmission, the grating reflectivity, or the efficiency of the CCD array detector; the overall detection sensitivity peaks at \( \sim 620 \) nm and is at least four times lower at the two extremes of the range displayed.

All features in these spectra can be assigned in terms of monatomic carbon species - neutrals and cations. Indeed, spectrum (a) exhibits all of the more intense documented \(^{25,26}\) transitions of C and C\(^+\) that lie in this wavelength range (suggesting a lack of specificity in the excited state production process), while only emissions associated with neutral C atoms are apparent in spectrum (e). Additional lines, \( e.g. \) at 501.76 nm, 495.76 nm and 459.45 nm, are transitions appearing in second order associated with, respectively, the \( \text{C}^+(2p^3s^2D^o \rightarrow 2s^12p^2^2P) \) multiplet at \( \sim 251.1 \) nm, the \( \text{C}^+(2p^13s^1\text{P}^o \rightarrow 2p^2^1S \) transition of atomic C at 247.86 nm, and the \( 2p^2^1D \rightarrow 2s^12p^1\text{P}^o \) transition of the C\(^{2+}\) dication at 229.69 nm. Comparing such spectra recorded at a range of positions in the plume and at a range of incident fluences reveals that:

(i) The C\(^{2+}\) feature is observed only at small \( d \) and at the highest \( F \).

(ii) The C\(^+\) emission line intensities are greater (relative to those associated with neutral C atoms) at smaller \( d \) and at higher \( F \).

(iii) Only neutral C emission lines are detected in regions remote from the focal spot and the purple shaft (\( e.g. \) at \( d \geq 3 \) mm for all \( \theta \leq 0^\circ \)).

Findings (i) and (ii) are in good accord with conclusions reached in a previous OES study of 193 nm laser ablation of graphite,\(^7\) though we also observe many emission lines at \( \lambda > 600 \) nm not observed in the earlier work, presumably because of detector insensitivity at these longer wavelengths. In accord with previous studies,\(^7,9,27\) we see no emission attributable to electronically excited \( \text{molecular} \) species in any of these spectra, though the characteristic Swan band (\( d^1\Pi_g \rightarrow a^1\Pi_u \)) emission of C\(_2\) is clearly visible when the ablation is carried out in background pressures of <1 Torr (<133 Pa) of
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He or Ar.\textsuperscript{28} OES, of course, only provides information about the (generally small) fraction of material that happens to be present in states that decay radiatively.

Nonetheless, preliminary QMS measurements performed with this apparatus\textsuperscript{28} of the energetic positively charged component of the plume generated by 193 nm PLA of graphite in vacuum reinforce the view that the plume is predominantly atomic in composition. These QMS investigations of the ionic fraction reveal just three peaks - a dominant peak with mass to charge ($m/z$) ratio 12 and weak features with $m/z$ 13 and 6, which are most readily attributed to $^{12}\text{C}^+$, $^{13}\text{C}^+$ and $^{12}\text{C}^{2+}$ ions, respectively (appendix 2).

4.4.2. Time resolved imaging of species specific emissions

The time evolution of the various emissions was investigated by time gated CCD imaging to measure TOF transients of wavelength selected emissions through a spatially localised and defined viewing column.

![Figure 4.6: CCD images of neutral C atom emission with $\lambda > 780$ nm centred at (a) 430 ns, (b) 630 ns and (c) 830 ns ($\Delta t=100$ ns), following 193 nm PLA of graphite in vacuum. 0 mm defines the front face of the graphite target, and the laser pulse is]
incident at 45° to the surface normal as indicated by the white arrow, with its long axis aligned along z. (d)-(f) show the corresponding plots of emission intensity versus distance along the surface normal (x).

Figure 4.6(a)-(c) displays time gated (Δt = 100 ns) intensified CCD images obtained by monitoring all detectable emission transmitted by a long wavelength band pass filter opaque to λ < 780 nm, recorded at three different times, following 193 nm PLA of graphite in vacuum. Again, the long axis of the laser output was aligned vertically in the laboratory frame. 0 mm defines the front face of the graphite target, and the laser pulse is incident at 45° to the surface normal. Analysis of the wavelength dispersed spectra (Figure 4.5) reveals that neutral C atoms are the sole carriers of such emission. Obviously, the measured images are 'squashed' 2-D projections of a 3-D cloud of emitting particles. Nonetheless, it is instructive to analyse such images in order to gain some measure of the radial velocity distribution. The right hand panels (d)-(f) show plots of emission intensity versus distance along the surface normal which, in this case, corresponds to the axis of maximum emission intensity. Figure 4.7 shows a plot of the median (i.e. centre-of-gravity) intensity position of a series of such images taken every 0.1 μs after the laser pulse versus delay time; the gradient of the line of best fit implies a propagation velocity for the emitting neutral C atoms, vₚ = 21 ± 1 km/s. Image analysis also allows estimation of the full width half maximum (FWHM) of the measured emission intensity profiles along any user selected slice, e.g. parallel and perpendicular to the propagation axis. Dispersion velocities δvₓ = 28 ± 1 km/s and δvᵧ = 24 ± 1 km/s were derived in this way, suggesting that the emitting C atom component within the ablation plume is propagating and expanding at comparable rates.
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Figure 4.7: Medians of the intensity distributions along $x$ ($\circ$), and FWHMs ($\triangleleft x$ ($\square$) and $\triangleleft y$ ($\blacktriangle$)), derived from time gated CCD images of the neutral C atom emission such as shown in Figure 4.6(a)-(c), recorded as a function of delay time after the laser pulse. The gradients of the lines of best fit give one measure of the propagation and dispersion velocities for the emitting neutral C atoms, $v_x = 21 \pm 1$ km/s, $\triangleleft x = 28 \pm 1$ km/s, $\triangleleft y = 24 \pm 1$ km/s.

Such behaviour should be contrasted with that displayed by the emitting C$^+$ ions, which we choose to monitor via the $4f^{2}\,^{2}F^0 \rightarrow 3d^{1}\,^{2}D$ transition at $\sim 426.71$ nm. This closely spaced doublet emission was isolated by imaging through a narrow band interference filter with peak transmission at 426.7 nm and 3 nm transmission FWHM. As Figure 4.8 shows, the C$^+$ emission following irradiation of the graphite target with the beam incident at $45^\circ$ to the surface normal is concentrated in a faster moving plasma ball that evolves along an axis roughly midway between the laser propagation axis and the surface normal. As with the neutral C atom emissions discussed above, analysis of such time-gated images provides a measure of the median propagation velocities of the emitting C$^+$ ions ($\bar{v}_+ \sim 40 \pm 1$ km/s along the $\theta = +22^\circ$ axis) and of the dispersion velocities parallel and perpendicular to this axis ($\triangleleft v_{\text{par}} = 11 \pm 1$ km/s and $\triangleleft v_{\text{perp}} = 16 \pm 1$ km/s, respectively).
Figure 4.8: Time-gated ($\Delta t =100$ ns) intensified CCD images of the 426.71 nm C$^+$ emission accompanying 193 nm PLA of graphite in vacuum. The three time windows shown are as in Figure 4.6 and, as in that figure, 0 mm defines the front face of the graphite target, and the laser pulse is incident at 45° to the surface normal and with its long axis aligned along z. (d)-(f) show the corresponding plots of emission intensity versus distance along the $\theta = +22^\circ$ axis.

Figure 4.9 shows images taken at three other angles of incidence (-11°, 30° and 60°). These serve to confirm the generality of the observation that the C$^+$ emission accompanying 193 nm ablation of graphite in vacuum (with the long axis of the laser output aligned along z) expands along an axis that is approximately centred on the angle bisecting the laser propagation axis and the surface normal. Previous studies$^{6,29}$ of pulsed laser ablation of graphite at both 193 nm and 248 nm have noted the different propagation characteristics of the C$^+$ and C emission components, but the directionality of the ball of C$^+$ emission was less evident.
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Figure 4.9: Time-gated intensified CCD images ($\Delta t = 100$ ns centred at a delay of 430 ns) of the 426.71 nm C$^+$ emission accompanying 193 nm PLA of graphite in vacuum, recorded at (a) 11°, (b) 30° and (c) 60°. As in Figure 4.6, 0 mm defines the front face of the graphite target, and the long axis of the output is along $z$. Each image has been cropped top and bottom for compactness of display.

Figure 4.10 provides a further exploration of this oversight. The ball of C$^+$ emission observed when the laser is incident at $\theta = 45^\circ$, but with the long axis of the output now aligned along $y$ (i.e. rotated so as to be perpendicular to the observation axis), is seen to propagate along $\theta \sim 10^\circ$ (i.e. much closer to the surface normal). Analysis of a time sequence of such images yields a mean propagation velocity, $v_+ \sim 40 \pm 1$ km/s along the $\theta = 10^\circ$ axis, and dispersion velocities parallel and perpendicular to this axis ($\delta v_{\text{par}} = 17 \pm 1$ km/s and $\delta v_{\text{perp}} = 11 \pm 1$ km/s), very similar to those measured with the laser pulse output aligned along $z$. 

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Figure 4.10: CCD images of the 426.71 nm C\(^+\) emission, recorded with the intensifier time gate (\(\Delta t=100\) ns) centred at (a) 430 ns, (b) 630 ns and (c) 830 ns, following 193 nm PLA of graphite in vacuum with the laser pulse incident at 45° to the surface normal. Again, the various images have been cropped top and bottom for display purposes and 0 mm defines the front face of the graphite target but, in contrast to Figure 4.9, the long axis of the laser output is now aligned along \(y\) (i.e. perpendicular to the observation axis).

Such species selective, time lapse images of the plume provide one direct, and very visual, means of monitoring the ablation plume and of estimating the propagation velocities of various of the constituents within the plume. These data can be compared with TOF measurements of wavelength selected emissions monitored using the fibre bundle, Spex monochromator and a fast PMT\(^{28}\). These measurements yield propagation velocities of \(42 \pm 1\) km/s for the C\(^+\) cations (measured for the 426.7 nm transition) and the C\(^{2+}\) dications and a propagation velocity of \(33 \pm 1\) km/s for the C atoms.

The propagation velocities for the C\(^+\) ions obtained by both methods are in good agreement with those estimated by Puretzky \textit{et al.}\(^{29}\) from analysis of time gated images of the fastest component in the total emission resulting from ArF laser ablation of graphite.
graphite in vacuum. The value recorded for the neutral carbon atoms are somewhat greater than that deduced from the time gated imaging studies shown in Figure 4.6 but still slower than the more localised C\textsuperscript{+} ion emission. Before discussing the significance and some of the limitations, of such OES studies, we first consider another type of measurement which can provide complementary information about the motion of positively charged particles in the expanding plume.

4.5. Faraday Cup Measurements

Figure 4.11(a) displays TOF transients of the positively charged material within the ablation plume, obtained using laser fluences of 5, 10, 15 and 20 J/cm\textsuperscript{2}, each incident at 45\textdegree{} to the surface normal, measured using the Faraday Cup detector located on the x axis with its front face at a distance \(d = 421.7\) mm from the target.

Figure 4.11: (a) TOF transients of the positively charged component of the ablation plume resulting from 193 nm PLA of graphite, in vacuum, using pulse energies of 5 (\textcircled{O}), 10 (\textsquare{}), 15 (\texttriangle{}), and 20 J/cm\textsuperscript{2} (\texttriangleleft). The solid curve through the 15 J/cm\textsuperscript{2} profile shows the result of a least squares fit in terms of Equation (4.1). (b) shows the velocity distributions that derive from the experimental TOF profiles.

The solid curve through the TOF profile recorded with 15 J/cm\textsuperscript{2} incident pulses serves to illustrate that the TOF profiles are each well described by a shifted Maxwell-Boltzmann velocity distribution of the form:
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\[ n(x,t) \propto t^{-3} \exp \left\{ -\frac{m}{2kT} \left( \frac{x}{t} - u \right)^2 \right\} \]  \hspace{1cm} (4.1)

where \( n(x,t) \) is the space- and time-dependent particle density, \( t \) is the TOF, and \( T \) (the local equilibrium temperature) and \( u \) (the flow velocity parallel the surface normal) are parameters to be floated in the fit. Such a function is generally assumed to provide a valid description of the TOF profile of ablated material in cases where a Knudsen layer is formed.\(^{19,30}\) Given previous estimates\(^8\) (from target mass loss measurements) that the C atom removal rate in these experiments is \( \sim 10^{15} \) pulse\(^{-1}\) when using 20 J/cm\(^2\) incident pulses, together with representative collision cross-section and velocity values of \( \sim 0.2 \) Å\(^2\) and 40 km/s, respectively, the requisite few collisions deemed necessary for Knudsen layer formation close to the surface will occur within the first few nanoseconds of the laser pulse. A more detailed discussion on the functional form of Equation (4.1) can be found in Chapter 3.

For analysis of the velocity profiles we define the most probable velocity \( (v_{mp}) \) as the velocity corresponding to the peak signal and the mean velocity \( (v_\text{m}) \) as the velocity separating the slower and faster halves of the total integrated signal. Comparing these two defined velocities Figure 4.12(a) gives an indication of the anisotropy of the velocity distribution. The velocity distributions that derive from these TOF profiles, displayed in Figure 4.11(b), show that both the total ion signal and the mean, \( v_\text{m} \), of each velocity distribution scale with increasing incident energy. These trends are summarised in Figure 4.12, where the mean ion kinetic energy has been calculated on the assumption that the charged particles have \( m/z \) 12.
Figure 4.12: Plots illustrating the variation of (a) total ion yield, (b) $v_{mp}$ ($\square$) and $v_+$ (O), and (c) the mean ion kinetic energy with pulse energy. The error bars in (a) show the reproducibility of five separate measurements of relative signal strengths as a function of pulse energy, each set of which has been arbitrarily normalised to unit signal at $F = 7.5 \text{ J/cm}^2$, while those in (b) and (c) are standard deviations (1$\sigma$) of the absolute velocities determined from, typically, five measurements at each energy. The solid curves in each plot are fourth order polynomial fits to the various data sets.

Interestingly, the plot of kinetic energy versus incident pulse energy (Figure 4.12(c)), though roughly linear, has a much shallower slope than that reported previously in the case of 308 nm ablation of graphite in vacuum.\textsuperscript{19} Figure 4.12(a) reveals ion production at very low incident fluences, in marked contrast to the OES measurements in which formation of electronically excited C$^+$ ions (i.e. the purple shaft) was evident only above a certain threshold energy, but the deduced velocities (e.g. $v_+ = 42.5 \pm 1 \text{ km/s for incident 20 J/cm}^2$ pulses) match well with those derived from the OES studies of C$^+$ emission. However, the CCD imaging studies also showed the
distribution of emitting $C^+$ species to be highly asymmetric about the surface normal - at variance with previous ion probe studies which suggested a far more uniform recoil distribution of the total ion flux.\(^8\)

![Image](image_url)

Figure 4.13: Plots showing: (a) the angular variation of the total positive ion signal arising in the 193 nm PLA of graphite in vacuum, using fluences of 5 (\(\triangle\)), 10 (O) and 20 J/cm\(^2\) (\(\Delta\)) and (b) the angular variation of the corresponding $v_+$ values. The smooth curves through the points are fits in terms of $\cos^q\theta$ distributions, with the best fit $q$ value indicated in each case; (c) and (d) show, respectively, the deduced centre of mass velocity, $u$, and the velocity dispersions parallel, $\delta v_x$ (\(\square\)), and perpendicular, $\delta v_y$ (O), to the surface normal, each as a function of incident pulse energy. The solid lines in these two panels are fits (using fourth order polynomials) to the data. The error bars are deduced as in Figure 4.12.

This paradox has been investigated further using the Faraday cup assembly. Experimental constraints mean that the axis along which the laser is incident and the ion detection axis had to be held constant. To investigate the variation in scattered ion flux with $\theta$ (\textit{i.e.} relative to the surface normal), it was thus necessary to vary the angle of
incidence on the target, by rotating the target assembly about the z axis, and measuring TOF transients such as those shown in Figure 4.11, as a function of both the laser pulse energy and its angle of incidence. Inevitably, this procedure must cause some change in the footprint of the focal spot on the target, and thus in the incident fluence at any given pulse energy. Nonetheless, as Figure 4.13(a) shows, the angular distribution of the total ion flux measured in this way, at all incident fluences, peaks at \( \theta = 0^\circ \) (in contrast to the OES observations) and conforms to a \( \cos^q \theta \) distribution with \( q \sim 5 \), thereby reinforcing previous conclusions\(^{24} \) that the distribution of the total ion flux distribution is considerably more isotropic than that of the \( C^+ \) ions evident in OES.

Given this grid of measured TOF spectra it is also possible to determine the way in which the velocity distribution varies with scattering angle. Knowing \( d \), it is possible to transform any measured TOF profile into the associated velocity distribution: Figure 4.13(b) shows that the median velocity, \( v_\text{m} \), also peaks at \( \theta \sim 0^\circ \) and exhibits an angular dependence that scales as \( \cos^q \theta \), with a best-fit \( q \) value that rises from \( -0.8 \) (for 5 J/cm\(^2\) pulses) to \( -1.2 \) (when using 20 J/cm\(^2\) pulses). It is also possible to fit each measured TOF profile in terms of a function analogous to Equation (4.1) but which now, since we are concerned with material ejection along axes other than the surface normal, involves velocity components both parallel and perpendicular (\( y \)) to \( x \), i.e.

\[
n(x_i, y_i, t) \propto A t^{-5} \exp \left\{ -\frac{m}{2kT_x} \left( \frac{x_i}{t} - u \right)^2 - \frac{m}{2kT_y} \left( \frac{y_i}{t} \right)^2 \right\}
\]  

(4.2)

Only \( T_y \) was floated when fitting TOF spectra recorded at \( \theta \neq 0^\circ \): \( u \) and \( T_x \) were clamped at the values determined from analysis of TOF spectra of ions ejected along the surface normal (\( i.e. \) using Equation (4.1)) at the same incident pulse energy. Best-fit values of \( u \), \( T_x \) and \( T_y \), and their variation with incident pulse energy, are shown in Figure 4.13(c) and (d). The corresponding full width half maximum (FWHM) velocity spreads parallel and perpendicular to the surface normal, \( \delta v_x \) and \( \delta v_y \), are deduced from the relationship

\[
\delta v_{x(y)} = \sqrt{\frac{8kT_{x(y)} \ln 2}{m}}
\]  

(4.3)
which follows from assuming that the velocity spreads in the $x$ and $y$ directions may be described by Gaussian functions. Reviewing these fits, and the plots shown in Figure 4.12 and Figure 4.13, we note for future reference that the total ion distribution in the plume resulting from 20 J/cm$^2$ excitation is well described by a shifted Maxwell-Boltzmann distribution propagating along the surface normal with a flow velocity, $u \approx 35$ km/s, and dispersion both parallel ($\delta v_x$) and perpendicular ($\delta v_y$) to this axis of $\approx 25$ km/s (FWHM). These values will be used later, in a simple model designed to account for the observed asymmetric C$^+$ emission.

### 4.6. Discussion of the results and model

Three different strategies, two based on OES$^{28}$, the other employing a Faraday cup, return similar values for the propagation velocity of the ionic component within the plume arising in the pulsed 193 nm laser ablation of graphite in vacuum.$^{31}$ Estimates of the propagation velocity of the neutral atomic C component determined by the two forms of OES show more variation, but consistently indicate that $\bar{v}_+ > \bar{v}_n$, in accord with previous studies.$^6,8,29$ Such observations are consistent with contemporary models of UV laser ablation in which the laser pulse induces localised surface excitation and rapid heating, leading to photo- and thermionic electron emission closely followed by ejection of positive ions, which are accelerated out of the focal volume as a result of Coulombic attraction (by the expanding electron cloud) and repulsion (by other ions at smaller $d$) before reaching some terminal propagation velocity.$^{32}$ Species ejected into the vacuum as neutrals are not subject to this Coulombic acceleration, whilst neutrals that result from gas phase ion-electron recombination in the denser (early time) regions of the plume will only experience such acceleration prior to neutralisation and thus attain a lower terminal velocity. More careful inspection, however, reveals other differences between the various measurements. Most notably, the CCD imaging studies suggest a far more localised distribution of emitting C$^+$ species (both in the radial and angular co-ordinates) than is indicated by either the present, or previous,$^8$ ion probe measurements.

Here we concentrate attention on possible mechanisms for producing the electronically excited species monitored via OES and, in particular, the origin of the
localised shaft of C\textsuperscript{+} emission. The radiative lifetimes of the various excited species are far shorter than the timescales over which emission is observed. Thus the emission observed at larger \( d \) must be from excited states that are populated post-ablation, in the gas phase, well after cessation of the pulsed laser excitation. Electron impact excitation (EIE) during plume expansion is one possible route for forming excited state species, the efficiency of which should fall with decreasing number density, and thus increasing \( d \). On this basis, EIE induced emission should be most efficient at small \( d \) and thus favour the slower moving particles. That being the case, OES might be expected to underestimate the actual plume propagation velocity. However, the EIE mechanism also requires the electrons and the atoms/ions to be proximate. Given that the electrons and ions have similar propagation velocities,\(^8\) both of which are greater than \( V_n \), it might follow that EIE would actually favour that sub-set of the total flux distribution that was propagating at similar speeds to the expanding electron cloud (i.e. the faster part of the neutral velocity distribution). EIE of C atoms and C\textsuperscript{+} ions is generally spin conserving.\(^{33}\) Thus, if EIE is the major route to the observed emissions, the fact that \textit{all} C and C\textsuperscript{+} emissions that fall within the monitored wavelength range are indeed observed (Figure 4.5) would imply the formation of both ground (triplet) and excited (singlet) C atoms in the ablation process. However, many of the emissions originate from very energetic excited states - \textit{e.g.} the \( ^4P^0 \) excited state of C\textsuperscript{+} responsible for the 432.2 nm and 359.1 nm emissions observed along the \( \theta = +22^\circ \) axis at short \( d \) lies 25.98 eV above the ground state ion and 37.25 eV above the ground state of neutral carbon. Such high levels of excitation are hard to reconcile with simple EIE induced by electrons propagating with mean kinetic energies in the meV range. Neither does an EIE mechanism provide a particularly obvious explanation for the observed highly localised C\textsuperscript{+} emission.

Another mechanism for forming electronically excited species is electron-ion recombination (EIR). This requires the presence of a third body to stabilise the recombination product, and should thus also be most important at small \( d \). EIR would encourage the conversion \( C^{2+} \rightarrow C^+ \rightarrow C \), in accord with the \( d \) dependence of these various species revealed by the OES studies. EIR will favour formation of Rydberg states with high principal quantum number, \( n \), since these recombination products require least energy transfer to the third body. Many of these Rydberg states will be formed not just with high \( n \) but also high \( l \) (where \( l \) is the orbital angular momentum
quantum number). Given the $\Delta l = \pm 1$ selection rule associated with allowed radiative transitions, these species can only radiate by a cascade mechanism. The initial steps in this cascade will involve Rydberg–Rydberg transitions at long wavelength; the spatial and temporal extent of the observed emission plumes would then reflect the time taken for the population in high $n, l$ states to cascade down into the observed emitting levels. The observation of emissions from excited states of both C and C$^-$ involving $\ldots$ng$^1$ and $\ldots$nf$^l$ configurations and of sequences like:

\[
\begin{align*}
2s^26g^1,^2G \xrightarrow{646.1\text{ nm}} & 2s^24f^1,^2F^o, & 426.8\text{ nm} \xrightarrow{2s^23d^1,^2D} & 2s^23p^1,^2P^o \\
658.2\text{ nm} \rightarrow 2s^23s^1,^2S
\end{align*}
\]

in C$^+$, encourage the view that radiative cascade accounts for the apparently delayed emission. Clearly, wavelength resolved OES measurements at longer infrared wavelengths would help in confirming the importance of EIR processes.

We now proceed to show how the localised C$^+$ emission, its directionality, and its sensitivity to the orientation of the laser output, are all explicable in terms of EIR following laser-plasma (rather than laser-target) interactions; indeed, we will show that such observations are a signature of laser-plasma interactions. To this end, we have implemented an approximate 2-D 'particle in the cell' type model which provides a rationale for the observed anisotropy of the C$^+$ emissions, and identifies various parameters which will tend to enhance or degrade such anisotropic optical emission from ablation plumes. Key features of the model are summarised in Figure 4.14.
As in the experiment, the front face of the target lies in the $yz$ plane, with the surface normal directed along $x$. All of the present calculations consider material ejection just in the $xy$ plane. This space is partitioned into a mesh of $75 \times 75$ rectangular grid cells, chosen so as to span the entire 'volume' into which sputtered material may have travelled by the cessation of the laser pulse. The pulse of laser radiation (of duration, $t = 20$ ns) is assumed to have a 'top hat' intensity distribution, in both space and time, and to be incident as a parallel shaft in the $xy$ plane, at an angle $\phi$ to the surface normal, so as to irradiate the target surface over a length distributed symmetrically about the point $y = 0$. This length is treated as 21 identical pixels of width $\delta y$, each of which serves as a source of ablated particles. All particles are treated as being identical, and each pixel within the length $\Delta y$ is assumed to contribute equally to the total ablation yield. In this simple model the ejected particle density from each pixel is distributed over 185 radial spokes, distributed uniformly throughout the angular range $-90^\circ < \theta < 90^\circ$.

Modelling of the laser interaction is sub-divided into 20 time steps, each with $\tau = 1$ ns, so as to span the entire laser pulse duration. During the first time step, $\tau_1$, a total of $N_1$ particles are ejected into the gas phase. Each source pixel contributes equally to $N_1$, and each contribution is given an overall velocity distribution (defined relative to its particular cell origin) the same as that deduced from analysis of the ion yield arising
Chapter 4: Laser ablation of graphite

when using 20 J/cm² pulses (i.e. $u = 35$ km/s, and with a Gaussian spread of 25 km/s (FWHM) in both the $x$ and $y$ directions. Each particle is ascribed an associated density, $\rho$, which is initially set to unity. This is necessary if, as here, the interest is in possible laser-plume interactions, since plume material in the column exposed to laser irradiation can attenuate the incident beam, and thus reduce the light intensity incident on the target and the ablation yield.\footnote{This attenuation is modelled using the Beer-Lambert expression,}

$$I(d) = I_0 \exp[-\alpha \rho(d)(d_{\text{max}} - d)]$$

where the absorption coefficient, $\alpha$, is assumed to be intensity independent, $\rho = \sum \rho_i$ is the local density within a grid cell distant $d$ from the focal region, and $d_{\text{max}}$ is defined as in Figure 4.14. In the limit that $\alpha \to 0$, the incident beam suffers no attenuation and $I(d_{\text{max}}) = I_0$.

During successive time steps, particles generated during all previous time steps will continue to propagate forward, and additional plume material will be produced as a result of the (attenuated) laser beam striking the target surface. To allow for possible plume absorption, the density $\rho$ in each grid cell is calculated at the end of each time step. Equation (4.4) is then used to calculate the intensity $I(d)$ incident on, and exiting from, each grid cell during the next time step. Consider two neighbouring cells along a radius within the irradiated column at positions $d_n$ and $d_{n-1}$ ($d_n > d_{n-1}$), containing respective densities $\rho_n$ and $\rho_{n-1}$. We define an excitation density $E_n(t)$ for the former grid cell as

$$E_n(t) = \rho_n [I(d_n) - I(d_{n-1})]$$

for the time step of interest and obtain a final, total excitation density for this cell via the summation $\sum_{t=0}^{20} E_n(t)$. Excitation decay is not included within the model. After 20 ns all gas phase material production and excitation is assumed to cease, and the velocities of all particles can be propagated to longer time to compare with the experimental observations.
Figure 4.15: Linear grey scale plots illustrating the calculated spatial distribution of total ablated flux in the $xy$ plane at $t = 0.5 \mu s$, for a laser pulse incident at $45^\circ$ to the surface normal (indicated by dashed line), with $\Delta y = 0.2$ mm and $\Delta t = 20$ ns, assuming $u = 35$ km/s, $\Delta v_x = \Delta v_y = 25$ km/s (FWHM) and three different 'strengths' of the absorption coefficient, $\alpha$ (such that the time integrated absorption corresponds to (a) 25, (b) 50 and (c) 75% of the incident light intensity, respectively). Panels (d)-(f) show the calculated distribution of excitation density, $\rho$, within the plume given these same three absorption strengths.

Figure 4.15 shows - in the form of linear grey scale plots - the spatial distribution of total ablated flux in the $xy$ plane predicted by this model at $t = 0.5 \mu s$, for a beam incident at $45^\circ$ to the surface normal, with $\Delta y = 0.2$ mm and $\Delta t = 20$ ns, assuming $u = 35$ km/s, $\Delta v_x = \Delta v_y = 25$ km/s (FWHM) and three different 'strengths' of the absorption coefficient, $\alpha$ (such that the time integrated absorption corresponds to (a) 25, (b) 50 and (c) 75% of the incident light intensity, respectively). Clearly, plume absorption reduces the overall ablation yield, but its effect is more obvious in the complementary plots (Figure 4.15(d)-(f)) showing the predicted distribution of excitation density within the plume. The anisotropy evident in these latter plots is reminiscent of that observed in the
time gated CCD images of the $C^+$ emission. Figure 4.16 shows the predicted variation in the anisotropy of the excitation density with the angle of incidence, $\phi$, of the exciting light pulse ((a), top panel), the focal spot size, $\Delta y$ ((b), centre panel) and the pulse duration ((c), bottom panel). The qualitative trends evident in (a) and (b) accord with the experimental observations (Figure 4.9 and Figure 4.10).

![Figure 4.16: Predicted variation in the anisotropy, via grey scale plots, of the excitation density, $\rho$, with (a), (top panel) the angle of incidence, $\phi$, of the exciting light pulse (indicated by dashed line), (b), (centre panel) the focal spot size, $\Delta y$, and (c) (bottom panel) the pulse duration, $\Delta t$. The default conditions apply for panel (b), 200 $\mu$m.](image)

The model calculations support the view that asymmetric plume excitation will generally be most evident in experiments which (as here) involve laser pulses incident at an angle away from the surface normal, of long time duration, and that are tightly focused such that the focal spot size on the target in the viewing plane ($\Delta y$) is small.
compared to the distance \((d_{\text{max}})\) that material can travel during the laser pulse. The simulations shown in Figure 4.16 indicate that the anisotropy will be reduced by expanding the size of the focal spot (as found experimentally - Figure 4.10), or by reducing the pulse duration. A more critical comparison between experimental observation and the model predictions indicates that the latter tend to underestimate the observed asymmetry of the \(C^+\) emission. Clearly, one contributor to this discrepancy is our use in the model of the 'asymptotic' particle velocity distribution, \(i.e.\) the distribution measured at long time, after formation of the Knudsen layer. Within the context of the model as posed, however, excitation of gas phase material will be most efficient in the very early part of the laser pulse, before the Knudsen layer is fully developed. Equation (4.2) with \(u \sim 0\) should provide a better description of the initial velocity distribution of the ablated material in the early time, low-density, near collision-free limit. The distribution of excitation density that results from assuming such a function is much more asymmetric. Clearly, a better match with observation can be obtained by making \(u\) a time dependent function, but we are satisfied that the present more limited calculation suffices to demonstrate the source of the observed asymmetry of the \(C^{+*}\) emission.

Figure 4.15 also serves to emphasise that such effects will be most evident where there is significant absorption by the plume. Experiments employing longer duration, high energy pulses will tend to produce a longer, denser column of ablated material through which the beam must propagate to reach the target; plume absorption is likely to be more important. Processes that might contribute to the attenuation of incident radiation by an ablation plume include scattering, and absorption - either resonant, or as a result of electron-neutral and/or electron-ion inverse Bremsstrahlung.\(^{35}\) As shown in section 4.3, both of these latter processes play an important role in the whole laser ablation process. The initial absorption can be ascribed to the resonance enhanced MPI process producing a relevant ionisation fraction. This will, in turn, instigate the IBE process resulting in additional absorption of the laser light and local ionisation of the plume. Thus the resonance enhanced two photon ionisation acts as a highly localised seeding mechanism for further ionisation. This process will be prevalent in the regions of the plume receiving the highest and most prolonged photon flux. These would be the regions identified as receiving the greatest excitation density in the simple model calculations reported above and, qualitatively at least, these correlate with the observed localised shaft of \(C^+\) emission.
4.6.1. Conclusions for the laser ablation plume characteristics

Electronically excited species (C atoms, and C\(^+\) and C\(^{2+}\) ions) in the plume accompanying 193 nm PLA of graphite in vacuum have been investigated by wavelength, time and spatially resolved OES, while the positively charged component has also been investigated using a Faraday cup detector. In addition, the attenuation of the laser light by the ablation plume has been studied by directly measuring and comparing the temporal profiles of the laser pulse after propagating through the ablation plume for different fluences.

The temporal and spatial extent of the optical emissions are explicable if it is assumed that the emitting species result from electron-ion recombination processes, and subsequent radiative cascade from the initially formed high \(n,l\) Rydberg states. The C neutral emission is observed to be distributed symmetrically about the surface normal, but the C\(^+\) emission is seen to be localised in a rather narrow solid angle between the laser propagation axis and the surface normal. However, the complementary Faraday cup measurements of the ion yield and velocity distributions, as a function of scattering angle and incident pulse energy, indicate that the total distribution of positive ions also peaks along the surface normal. The velocity distributions so derived are used as input for a simple two dimensional model which provides a rationale for the observed anisotropy of the C\(^+\) emission in terms of preferential multiphoton excitation and ionisation of C species in the leading part of the expanding plasma ball that are exposed to the greatest incident 193 nm photon flux, and subsequent electron-ion recombination and radiative decay. The attenuation experiments studied with the laser beam incident on the surface normal indicate a strong absorption of the laser light at fluences above 12 J/cm\(^2\). This is the fluence regime where a bright purple plasma ball becomes prevalent in the optical emission. The results support an initial ion creation mechanism involving resonance enhanced multiphoton ionisation with, at higher fluences, sequential photon absorption by the plasma resulting from electron-ion IBE. The reported results from the different applied techniques are in very good agreement with each other and with results reported in related studies.\(^6,7\)
4.7. Deposition of Diamond Like Carbon films

The deposition of DLC films was the subject of previous studies in our group.\textsuperscript{28} These results are summarised so as to provide a complete story. The films were typically deposited from graphite, although we have also investigated DLC film production via ablation of CVD diamond.\textsuperscript{24} A previous optical emission study of the ablation plumes from both target materials revealed that the ablation characteristics of the materials are very similar. This is explained by assuming that the incident laser light induces local melting of the graphite and the CVD diamond target surfaces prior to ablation. Thus the CVD diamond surface undergoes a 'graphitisation' and, thereafter, shows the same ablation characteristics as graphite itself.\textsuperscript{24}

The films were characterised by UV-VIS and Raman spectrometry and their field emission characteristics were investigated.

4.7.1. Deposition of DLC films

193 nm laser fluences required for production of high quality DLC films from graphite were determined to be in the range of 12.5 J/cm\textsuperscript{2} and 25 J/cm\textsuperscript{2}. Obtaining sufficiently sharp SEM cross-sectional images of the DLC films produced in this work to allow reliable estimation of the film thickness proved difficult. However, guided by our previous studies of the 193 nm PLA of graphite in vacuum\textsuperscript{24} (which suggested deposition rates of \(-7\) pm pulse\textsuperscript{-1}), we estimate that the 'typical' film deposited here using 20 J/cm\textsuperscript{2} pulses, 10 Hz repetition rate and 15 minutes duration had a thickness of \(\sim50\) nm. SEM imaging showed severe delamination of films deposited from both graphite and CVD diamond targets when using longer durations, or higher pulse energies, as shown in Figure 4.17.
The deposited films are characterised with UV-VIS and Raman spectrometry. Typical spectra obtained by the two techniques are given in Figure 4.18. The results show that the films are typical DLC films, and their characteristics can be compared with the studies given in references 7.

The UV-VIS spectrum shows that absorption of the film stretches out into the visible region ($E < 3$ eV) and that the DLC films do not exhibit a well-defined optical band gap. A general procedure to estimate the band gap involves extrapolation of the long wavelength part of such plots of absorption coefficient versus energy (or frequency) and determining the energy at which this trend-line intercepts the energy axis. It is clear that almost any band gap value could be obtained by extrapolating the appropriate part of an absorption spectrum such as shown in Figure 4.18(a). Such UV-VIS spectra give convoluted information about the refractive index and the extinction coefficient of the material. Ellipsometry offers a better method for determining these two quantities directly. Ong et al. 7 have reported values of 2.1 - 2.3 eV for the optical band gap measured by ellipsometry for DLC films deposited under similar conditions to those used in the present work.
Figure 4.18: (a) typical UV-VIS spectrum of a film deposited from graphite on a quartz substrate at 25 J/cm². Typical Laser Raman spectra, at an excitation wavelength of 514 nm of (b) the deposited film (c) the irradiated part of the graphite target and (d) the virgin graphite target as comparison. The total signal in (c) and (d) are plotted on the same vertical scale for comparison. All the Raman spectra are baseline corrected, the procedure is shown in (e). The peak at 960 cm⁻¹ in (b) is a feature associated with the Si substrate.

The Raman spectrum of the deposited film material is given in Figure 4.18(b) together with Raman spectra for graphite, pre- and post- ablation (c) and (d).
spectrum taken from an irradiated graphite surface is distinctively different from that of the virgin graphite surface given for comparison. The former shows clear broadening, reflecting disordering of the lattice structure. This we attribute to localised melting of the graphite lattice under the influence of the high photon flux, though it should be noted that some redeposition of sputtered carbon atoms and ions occurs also, resulting in deposition of a thin DLC film on the target surface.

The Raman spectrum in Figure 4.18(b) is consistent with good quality hydrogen-free DLC, the peak around 960 cm\(^{-1}\) is due silicon in second order (fundamental frequency \(\sim\)520 cm\(^{-1}\)). Quantification of these films was the subject of a more involved earlier study,\(^{28}\) in which the DLC features were fitted to a Breit-Wigner-Fano lineshape (as discussed in reference 36) to yield estimates of the sp\(^3\) fraction in the deposited films of > 60%.

As mentioned previously we also compared characteristics of the films deposited from 193 nm ablation of graphite and CVD diamond. Figure 4.19 shows six laser Raman spectra. (a) and (b) are of the as-grown free-standing CVD diamond and the high density graphite targets, respectively, (c) is of the focal area on the CVD diamond film surface post-ablation, while (d) and (e) show spectra of the DLC films grown on Si by PLA of these respective targets. These five spectra were all recorded using 488 nm Ar\(^+\) laser excitation. (f) displays a Raman spectrum of the same film as in (e), but recorded using 325 nm excitation. Clearly, laser Raman spectroscopy of the deposited DLC films ((d) and (e)) provides yet more support for the view that there is little difference in the ablated material resulting from 193 nm irradiation of graphite and CVD diamond. Some rationale for this finding comes from comparing spectra (a), (b) and (c). The strong 1332 cm\(^{-1}\) peak in (a) highlights the high quality of the CVD diamond surface, yet post-ablation (spectrum (c)) laser Raman spectroscopy shows little evidence for diamond. All of the present observations are explicable by assuming that the initial stages of the PLA of CVD diamond in vacuum at 193 nm involve very rapid localised surface graphitisation prior to material injection into the gas phase.
Figure 4.19: Raman spectra taken using 488 nm Ar$^+$ laser excitation of (a) and (b) a virgin CVD diamond and graphite target, respectively, (c) the laser irradiation region of CVD diamond post-ablation, (d) and (e) films grown from CVD diamond and graphite, respectively and (f) the same film as (e) but the Raman spectrum is recorded with 325 nm laser excitation wavelength.

The differences between spectra (e) and (f) merit comment. The strong feature centred in (e) at a Stokes shift of $\sim$965 cm$^{-1}$ is a signature of the Si substrate. The relative showing of this peak decreases with decreasing excitation wavelength (see also reference 37), reflecting the increasing absorption coefficient of the deposited DLC coating at shorter wavelengths and the consequent reduction in the penetration depth achieved by the Raman exciting laser. Closer inspection of these spectra, and of those taken previously for similar DLC films using 632.8 nm He-Ne laser excitation, reveals a noticeable and systematic shift in the peak of the broad asymmetric Raman profile traditionally associated with DLC. from $\sim$1485 cm$^{-1}$ (632.8 nm excitation), through $\sim$1560 cm$^{-1}$ (488 nm, (c)) to $\sim$1595 cm$^{-1}$ (325 nm, (f)). This suggests that, as is widely recognised for the case of polycrystalline CVD diamond, the detailed form of the
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Raman spectrum obtained for any given DLC film will be sensitive to the excitation wavelength used.²⁹

4.7.2. Field emission characteristics

Figure 4.20 shows measurements of emission current (I) as a function of bias voltage (V) for DLC films grown from both CVD diamond and graphite targets. Such I-V curves were measured by ramping V up and down, repeatedly (sweep rate ~25 V s⁻¹); the reproducibility improved after the first few up-down cycles, but SEM analysis revealed that this 'conditioning' does affect the film morphology in the immediate vicinity of the emission sites. An SEM image illustrating surface modification after field emission is given in Figure 4.21. The surface shows severe damage but, as can be derived from the SEM picture, the damaged area shows better conductivity than the deposited film (the damaged area is brighter), indicating better transmission of electrons to the surface for field emission.

Figure 4.20: I-V curves for hydrogen-free DLC films grown on Si(100) by 193 nm PLA of (a) CVD diamond and (b) graphite obtained using 20 (□), 40 (O) and 60 µm (Δ) anode-surface separations.
Measurements were made at three different anode-surface separations (20, 40 and 60 µm), at several sites on each film, and for at least two films deposited from each target material. The DLC films derived from these two sources show very similar threshold voltages (50 V/µm) but, once above the threshold, films grown from CVD diamond appear to show a steeper slope, implying larger dI/dV. Such behaviour may correlate with the density of larger (>1 µm wide) macroparticles in the film, which both optical microscopy and SEM images suggest is considerably higher in the case of the film deposited from CVD diamond. Such a finding, which at first sight appears counter-intuitive given the proposed mechanisms for macroparticle ejection and the higher density and lower porosity of diamond, might well be dependent on the CVD diamond growth rate. Diamond samples such as those used here, deposited at high growth rates using a plasma jet, are likely to contain more voids (and thus trapped gas pockets) than the smaller grain size films produced in most low power CVD reactors.

4.7.3. Deposition of C:S films

The deposition of sulphur containing DLC films (henceforth C:S films) at room temperature was also attempted. The main challenge encountered in this part of the project was the target configuration. The first attempts to make a C:S containing target involved cold pressing a mixture of graphite and sulphur powder. Even at high pressures (~ 10 metric tonnes/cm²) this mixture remained as a powder. The powder
could be transformed to a solid by adding adamantane to the mixture, but adamantane has a high vapour pressure and the resulting disk fragmented when placed under vacuum. Hot pressing of the powders was not considered to be a viable production route, because of the huge differences in melting point of the two materials. Finally, the target assembly given in Figure 4.22 was used. It consists of a normal HOPG graphite target with a small strip of sulphur attached to the graphite target surface. The sulphur strip was prepared from pure (99.9 %) sulphur powder either by cold pressing or by heating the powder till melting temperature (213 °C) and allowing the resulting melt to resolidify. The target is mounted on a rotation stage set to rotate at 1 rpm. Use of such a conceptionally simple approach has also been reported in studies of the co-deposition of metals and DLC; 40,41 these latter studies demonstrate successful incorporation of the metals as dopants within the DLC film. The dopant concentration can easily be changed and selected by changing the strip width, which changes the aspect ratio (the relative amounts of the two materials exposed to the laser irradiation), though some preliminary studies are usually needed to establish the respective ablation rates of the two materials.

Post deposition EDAX analysis of the graphite target showed no significant redeposition of sulphur on the graphite surface (or C on the sulphur strip), implying that the substrate surface is subjected to either a flow of carbon or sulphur particles, dependent on the position of the laser footprint on the target.

![Figure 4.22: Target arrangement used when ablating a C:S target.](image)

The pressure in the vacuum chamber was observed to rise from the initial deposition pressure of $5 \times 10^{-6}$ Torr to much higher values ($1 \times 10^{-4}$ Torr) when
depositing C:S films with this target assembly; when ablation stopped the pressure rapidly dropped back to its base value. Such a pressure rise is much higher than that observed during ablation of graphite and deposition of normal DLC films. This observation has been investigated further by using the mass spectrometer in Residual Gas Analysis (RGA) mode. The mass spectrometer was chosen to operate in off-axis alignment (the axis defined by the Mass Spectrometer is at 90° with the surface normal of the target) with the entrance nozzle at a distance of 250 mm to detect gaseous species formed during ablation, with the substrate positioned 5 cm from the target. The kinetic energy of species detected under these experimental conditions is thermal. The mass spectrometer was operated with a cage voltage of 3 V and the ioniser voltage was set to 20 V so as to ionise the neutral molecules without fragmenting them by high energy electron impact. Figure 4.23 shows mass spectra of the residual gas in the chamber (a) when no ablation is occurring and (b) when ablating a C:S target (4 % S aspect ratio). Both show clear peaks at m/z 18 (H₂O), 28 (N₂) and 44 (CO₂) and look similar except for the additional signal at m/z 76 when ablating C:S targets. This mass corresponds to CS₂, which is a probable stable, volatile product of C:S ablation. A small increase of the signal at m/z 34 amu is also noticeable, attributable to H₂S. No peaks were observed at higher masses (m/z > 100 amu).

![Mass spectra of the residual gas](image)

Figure 4.23: Mass spectra of the residual gas (a) no ablation (b) C:S ablation for a laser fluence of 10 J/cm².
Additionally, the time dependence of the relative gas concentration can be studied by continuously monitoring the signal associated with the various m/z ratios. This was done for two different aspect ratios, namely 4 % S (top trace) and 24% S (lower trace) and a fluence of 10 J/cm². Figure 4.24 shows that the observed CS₂ signal coincides with the ablation event, particularly with the ablation of graphite. The signal drops when sulphur is ablated. The total yield of CS₂ also scales with the aspect ratio. The absolute scale in Figure 4.24(a) is 1500 counts while that in Figure 4.24(b) is 3500 counts. The temporal profile of the CS₂ signal drops steeply during the graphite ablation stage in the case of low S:C aspect ratio, but with the higher S:C ratio target this trend is much less noticeable. The dependence of the water signal during ablation is plotted in Figure 4.24(c). This shows a long time variation but as expected, is insensitive to whether C or S is being ablated. The dependence of the 34 amu (H₂S) signal was also studied and gave a temporal dependence similar to, but less explicit than, that of the CS₂ signal.

The dependence of gaseous CS₂ formation during the ablation event can be rationalised as follows. Since the EDAX measurements indicated that little or no significant re-deposition of sulphur on the graphite target surface and vice versa, production of nascent CS₂ from the target surface as a side product of the ablation process is very unlikely. Gas phase recombination of the ablation products during flight is also unlikely since, at any one time, essentially pure graphite or pure sulphur will be ablated. Spikes in the m/z 76 signal observed at the boundary of the graphite and sulphur areas (more noticeable in the 4 % aspect ratio data) might be attributable to co-ablation of carbon and sulphur in a single shot because of the finite size of the laser footprint.
Figure 4.24: Temporal profiles of the m/z 76 signal for S:C aspect ratios of (a) 4% and (b) 24%. The dashed lines indicate the different subdivisions of the process; start and stop indicate the beginning and end of the laser ablation process, respectively, and G and S indicate the periods when graphite and sulphur were irradiated by the laser, respectively. (c) shows the temporal profile of the m/z 18 (H₂O) signal during this ablation cycle.

The CS₂ gas products are more likely to be generated on the substrate surface and, unavoidably, also on the walls of the ablation chamber, as a by-product of the pulsed laser deposition. The approach of alternately ablating sulphur and graphite has the
major disadvantage that the deposition will result in layered structures. So, just after tracking the graphite target, the substrate surface will consist of a carbon rich film, and vice versa. As shown in section 4.7.1, the carbon films deposited under the given experimental conditions are dense DLC films with a high (> 60 %) sp³ fraction. The surface displacement energy of a sulphur atom (2.88 eV/atom) is much lower than for a carbon atom (7.8 eV/atom, assumed to be in a graphite lattice) which makes it much more feasible for a sulphur atom to be sputtered by a transient high energy flow of carbon atoms than vice versa. Sulphur atoms ejected into the gas phase during C atom bombardment will likely recombine to form CS₂.

Films were deposited for 15 minutes using different fluences (5-20 J/cm²) and S:C aspect ratios (7-16 %) and were characterised with Auger spectroscopy and XPS, Raman spectroscopy and SEM. Compositional results obtained from Auger spectroscopy and XPS analysis are given in Table 4.1.

<table>
<thead>
<tr>
<th>S: C Aspect Ratio</th>
<th>7 %</th>
<th>16 %</th>
</tr>
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<tbody>
<tr>
<td>Fluence</td>
<td>Auger</td>
<td>XPS</td>
</tr>
<tr>
<td>5 J/cm²</td>
<td>27</td>
<td>16</td>
</tr>
<tr>
<td>10 J/cm²</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>15 J/cm²</td>
<td>9</td>
<td>10</td>
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Table 4.1: S content (percent) in the deposited C:S films measured by Auger and XPS, the values were deduced from integrating under the peaks attributable to C or S and corrected for the relative sensitivity of the methods to the different species.

The techniques show significant differences in the absolute values of the % S within the film, but they show the same trend, namely:

(i) The percentage of sulphur is dependent on the initial aspect ratio on the target. This is self-evident, since the more sulphur is ablated, the more sulphur is deposited on the substrate.

(ii) The amount of carbon in the film scales with the fluence. This can be explained by the hugely different melting temperatures of both materials, sulphur melts at 486 K while carbon melts at 4300 K, which makes graphite a much more difficult material to ablate than sulphur.
(iii) The total amount of sulphur in the deposited film is always higher than the aspect ratio (by a factor of 1.4-2.8, depending on the fluence), again reflecting the different melting temperatures.

The films were also analysed by Raman spectroscopy in an effort to obtain insight into the bonding within the films. Raman spectra of the deposited films are given in Figure 4.25, and Figure 4.26 compares the Raman spectrum of a deposited film with that of sulphur. The films deposited with lower C:S ratios gave a very small Raman signal, while the Raman spectrum of films deposited with higher C:S ratios were essentially indistinguishable from those of undoped DLC films. None of the deposited films exhibited features characteristic of elemental sulphur (given in Figure 4.26(a)).

![Figure 4.25: Raman spectra of C:S films grown on Si substrate (Si is responsible for the 960 cm\(^{-1}\) feature), as summarised in Table 4.1, with (a) 16 % aspect ratio / 5 J/cm\(^2\), (b) 16 % aspect ratio / 10 J/cm\(^2\), (c) 7 % aspect ratio / 5 J/cm\(^2\), (d) 7 % aspect ratio / 10 J/cm\(^2\) and (e) 7 % aspect ratio / 15 J/cm\(^2\), respectively.](image-url)
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Figure 4.26: (a) Shows a Raman spectrum of sulphur, which can be compared with that of the film with the highest sulphur content (16 % aspect ratio / 5 J/cm²) shown in (b). The 520 cm⁻¹ feature in (b) is due to the fundamental of the Si substrate.

The results can be interpreted as follows. The films with higher sulphur content exhibit only a small DLC signal. This could be attributable to the thickness of the film. Films with a high sulphur content are typically grown with low fluences (5-10 J/cm²) and consequent at low deposition rates. A second explanation might be that films grown with a high sulphur (40 %) content should no longer be considered as DLC films. If we assume that the sulphur is incorporated within the DLC lattice, such high doping percentages will create a new material with different structural characteristics. Films with lower sulphur contents show a Raman spectrum more typical of DLC, comparable to the spectra reported earlier (section 4.7.1). The absence of strong sulphur features, (compare Figure 4.26(a) and Figure 4.26(b)) indicates that even the S rich films do not contain any extensive S networks.

Closer inspection of the films with SEM shows that the films are smooth but incorporate some needle shaped macroparticles as revealed in Figure 4.27. These tube-like structures are not observed when growing pure DLC films, but are, to some extent, evident in all the films grown with sulphur doping, indicating a general, sulphur
assisted, mechanism for their formation. However, EDAX mapping of the surface of the film indicates that these structures are not pure sulphur.

Figure 4.27: Needle-like structures in the C:S film (16 % aspect ratio / 15 J/cm² /RT) images at high magnification to show the microstructure of the tube-like macroparticles.

4.7.4. Conclusions for film deposition

193 nm ablation of graphite in vacuum has been studied and shown to lead to DLC films of high quality. The fluence dependence of the deposition process was the subject of an earlier study; the quality, as determined by laser Raman spectrometry, of the produced films remains constant throughout the fluence region.²⁸

The 193 nm PLA of both CVD diamond and graphite samples, in vacuum, have been compared and contrasted - both from the perspective of the ablation plume and by investigation of the resulting DLC films deposited on Si(100). The composition and propagation of the plumes from both targets have been probed via wavelength, spatially and temporally resolved studies of the plume emission and by Langmuir probe TOF methods and found to be very similar, thereby extending and conforming results reported in a previous study.²⁸

The deposited DLC films grown on Si substrates maintained at room temperature were studied by laser Raman spectroscopy, by both optical and scanning electron microscopy, and their field emission characteristics investigated. Again, similarities outweigh the differences, but DLC films grown from ablation of the diamond target
appear to show steeper $I/V$ dependencies once above the threshold voltage (~ 50 V μm) for field emission.

The results of the sulphur doping study show that it is possible to deposit sulphur containing DLC films with percentages ranging from 10 to 40 % sulphur. The observed pressure rise during deposition indicated a gas formation mechanism, which we attribute to CS$_2$ formation as a result of reactive sputtering of previously deposited sulphur from the surface of the substrate and the vacuum chamber walls. Interestingly, CS$_2$ formation is also observed in the CVD of sulphur containing diamond films from CS$_2$/H$_2$ + CH$_4$/H$_2$S/H$_2$ gas mixtures, as shown by our laboratory.\(^4\)

The Raman spectra of the sulphur doped films showed the characteristic DLC feature in the case of films grown with low sulphur concentrations, but this feature becomes less pronounced in the case of films grown with higher sulphur content. The surface of the films appears smooth, but some needle-shaped macroparticles are embedded. These macroparticles appear to be a characteristic feature of films formed by co-deposition of carbon and sulphur.

### 4.8. References

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Chapter 4: Laser ablation of graphite


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26 A. R. Striganov and N. S. Sventitskii, Tables of Spectral Lines of Neutral and Ionised Atoms, IFI/Plenum, New York (1968)

Chapter 4: Laser ablation of graphite

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5. Nanosecond ArF Pulsed Laser Ablation of Zinc Oxide and Pulsed Laser Deposition of Thin Zinc Oxide Films

5.1. Introduction

5.1.1. Applications of zinc oxide

Zinc oxide is a material with wide applications, ranging from its use as a pigment in paints and an additive in sunscreen to highly technological applications as a catalyst and in solid state devices. These applications all arise from the unique properties of the material.

Zinc oxide is a wide band gap semiconductor (band gap = 3.4 eV) which makes it an excellent visible transparent, UV absorbent material. This, together with its low toxicity, makes it an ideal material to use in sunscreens as a UV blocking element. The wide band gap also appeals to the semiconductor industry. The material can be readily modified to produce an n-type doped semiconductor. The most commonly used n-type dopants are aluminium and gallium. Recent developments in the field also yielded p-type doped zinc oxide via doping with arsenic, which is a step towards the production of p-n junctions of zinc oxide. It is hoped that such p-n junctions will find use as laser diodes, with their lasing transition in the blue. Doping also increases the conductivity of the material. Since zinc oxide is intrinsically transparent to visible light this allows production of a conducting visible transparent material. Such materials are used as electrodes in solar cells and in phosphor screens. Thin films of zinc oxide also exert a capability for second harmonic generation suggesting interesting photonic applications for the material. A very recent development is the use of zinc oxide as a lasing medium itself. This property has been illustrated in thin films and nanotubes of zinc oxide.
5.1.2. Laser ablation of zinc oxide and deposition of thin films

In this chapter the two aspects of the process, namely the pulsed laser ablation of ZnO and the deposition of ZnO thin films will be studied in detail. Pulsed laser ablation in vacuum will be studied to obtain a detailed picture of the governing processes for this specific material and, where necessary, comparison with the ablation of other materials will be made, to support the interpretations of the behaviour. Ablation behaviour in a background gas will be studied also, since optimal film deposition is found to occur if a small background pressure of oxygen is used.

The investigation of the pulsed laser deposition will concentrate on the optimisation of the deposition parameters, i.e. substrate temperature and background pressure of oxygen. The deposited films are analysed by numerous techniques to obtain a detailed picture of the specifics of the film growth under the given conditions. The main properties of interest are; crystallinity and alignment (studied by XRD and TEM), UV-visible transparency and band gap (studied by UV-VIS spectrometry). Results on the properties of aluminium and gallium doped ZnO films will be reported also.

In addition, results of ab initio theoretical calculations of the bulk and surface structure of ZnO will be presented and discussed within the framework of presently accepted theories of oxide surfaces.

5.2. Experimental

The experimental set-up has been discussed in Chapter 2. Specific for the ZnO set-up is the necessity to grow films in small background pressures of oxygen and nitrogen gas and on a heated substrate (≤ 500 °C). To obtain a small background pressure of oxygen (5 mTorr - 0.5 Torr), pure oxygen was bled through a mass flow controller at a flow rate of 0.5 sccm.

The plasma properties were measured via OES and Langmuir Probe measurements. The first technique yields relative measures of the plasma excitation and absolute figures for the velocity of the emitting transient species. The latter technique monitors the transient behaviour of the electrons in the ablation plume. Combining results of the two techniques provides a consistent picture of the ablation behaviour of ZnO.
The target morphology changes during ablation. The unablated ZnO is yellowish white and insulating while the ablated area turns grey and conducting in accordance with reference 10. More information about the target surface morphology after ablation will be provided in section 5.3.4. The experiments are all performed on a preablated track on the target to try to minimise any effects of this changing morphology.

5.3. Pulsed laser ablation of zinc oxide

The pulsed laser ablation of ZnO was studied in vacuum and in a small background pressure of oxygen via optical emission spectroscopy and Langmuir/Ion probe measurements. In the next paragraphs the ablation behaviour of zinc oxide in vacuum, then in small background pressures of O₂ will be discussed.

5.3.1. Time integrated optical emission spectroscopy in vacuum

The time integrated, wavelength dispersed UV-visible optical emission of the plume accompanying 193 nm ablation of ZnO, originating from the ablation spot and viewed along the surface normal, was studied to deduce information about the plasma formation and the ablation behaviour. The plasma formation is dependent on the laser fluence, and the observed optical emission varies with distance from the target surface. Optical emission spectra obtained in this way are compared with a spectrum arising from ablation of pure zinc. Optical emission spectra observed at laser fluences of 4 J/cm² and 20 J/ cm², at a distance of 5 mm along the surface normal are given in Figure 5.1, together with a corresponding spectrum taken using a pure zinc target (20 J/cm² and 5 mm).
Figure 5.1: (a) and (b) Emission spectra of ZnO (c) emission spectrum of Zn all measured at a distance of 5 mm from the target, (a) and (c) for a fluence of 10 J/cm² and (b) for a fluence of 4 J/cm². The observed lines are listed in Appendix 6 and a Grotrian diagram for Zn / Zn⁺ is given in Figure 5.6. SO indicates lines appear in second order.

The brightest emission lines are the 328.2, 330.3, 334.5 and 636.2 nm lines of atomic zinc, the 491.3 and 492.5 nm lines of the zinc cation and the 777.2 nm line of the oxygen atom. Comparison between the zinc oxide and zinc spectra shows that most of the emission lines in the spectrum of zinc oxide can be attributed to zinc atomic and cationic emission. The observed lines attributable to oxygen are all associated with the neutral atom. Even at the highest laser fluence employed no optical emission attributable to oxygen cations is observed.

The emission arising from the ablation of Zn and ZnO has also been compared via a correlation diagram. In this diagram the intensities of various features in the emission spectrum from ablation of zinc are plotted against the corresponding intensities in the emission from ablation of zinc oxide; this is shown in Figure 5.2. Points lying on the x-axis indicate those lines that only appear in the emission from ablation of zinc oxide. These points can all be associated with points from line emission from atomic oxygen.
The dense region close to the origin is related to less intense emission lines and background noise. The points with higher \((x,y)\)-values correspond to the more intense emission lines. The ellipses collect together points on the correlation graph associated with a particular transition. The regions with a lower gradient (closer to the \(x\)-axis) are related with optical emission that is more prevalent in the ablation of zinc oxide than in zinc and vice versa. A straightforward conclusion to be drawn from this correlation diagram is that the intensity of specific emission lines arising from ablation is dependent on the composition of the plume, the additional oxygen existing in the ablation plume of \(\text{ZnO}\) is also affecting the relative intensity of the \(\text{Zn}\) and \(\text{Zn}^+\) lines. More quantitatively, it can be seen that the 636.2 nm line of atomic \(\text{Zn}\) is relatively more intense in the ablation of \(\text{ZnO}\) than \(\text{Zn}\), while the 776.0 and 761.4 nm lines of \(\text{Zn}^+\) appear with greater relative intensity in the ablation of \(\text{Zn}\) than \(\text{ZnO}\).

![Correlation diagram between the emission line intensities in the spectrum from \(\text{Zn}\) and \(\text{ZnO}\) targets at the distance of 5 mm from the target, along the surface normal and a fluence of 10 J/cm\(^2\). The ellipses indicate the emission lines associated with the points on the correlation graph.](image)

Figure 5.2: Correlation diagram between the emission line intensities in the spectrum from \(\text{Zn}\) and \(\text{ZnO}\) targets at the distance of 5 mm from the target, along the surface normal and a fluence of 10 J/cm\(^2\). The ellipses indicate the emission lines associated with the points on the correlation graph.
Comparison between spectra obtained using the ZnO target at two different laser fluences reveals that the total optical emission increases with laser fluence, but that the relative emission intensities of different emission lines is dependent on the fluence. For example, the relative emission intensities of zinc atom and cation lines are highly dependent on the laser fluence used.

Further illustration of the fluence dependence of the relative intensities of different emission lines is given in Figure 5.3. The relative intensity of the emission lines is normalised and averaged over a few lines as indicated in the caption. From this figure it can be concluded that the relative optical emission intensity is species dependent. Different emission lines of atomic zinc show a linear dependence on the incident fluence, whereas the emission arising from transitions within a Zn⁺ varies non-linearly on the fluence. Emission arising from transitions within the oxygen atom shows a linear dependence on the incident laser fluence, although the error bars are larger (compared with the zinc lines). This could be explained by the poor transmission efficiency of the spectrometer and the low quantum efficiency of the detector at the long wavelengths at which the oxygen lines appear.

The distance dependence of the optical emission was studied also, and a summary of the results is given in Figure 5.4. The time integrated optical emission shows typical decay behaviour with increasing distance at a fluence of 20 J/cm². The dependence of the optical emission on distance is again species dependent. Zinc ion lines decay much faster than zinc and oxygen atom lines. The intensity versus distance plot for oxygen atom emission lines is comparable to that of the zinc atom emission lines.
Figure 5.3: Fluence dependence of the optical emission for (a) Zn atom, (b) oxygen atoms and (c) Zn$^+$ ions arising in the 193 nm laser ablation of a ZnO target. The lines considered for obtaining the plot are the 468.0, 472.2, 481.0 and 636.2 nm lines for Zn, the 777.2, 844.6 and 926.1 nm lines for O and the 491.1 and 492.4 nm lines for Zn$^+$. The maximum absolute intensity of each optical emission line was normalised to one. The fitted curves serve to indicate the trends; the curves for (a) and (b) are straight lines, while the fitting curve for (c) is a third order polynomial; this order polynomial provided the best fit to the data.
Figure 5.4: Distance dependence of the emission lines at a fluence of 20 J/cm². The selected emission lines for the plot are the 481.1 nm line for Zn, the 844.6 nm line for O and the 492.4 nm line for Zn⁺. The absolute intensity values for each of the emission lines are normalised to one at d = 3 mm. Other optical emission lines for the same species give the same distance dependence.

The optical emission lines observed at short distances (Figure 5.5) appear broadened. This we attribute to an intrinsic pressure broadening, due to the high charge density in the region just in front of the target. In addition, the lines are seen to be superimposed on a continuous background emission. This background emission can be attributed to either Bremsstrahlung of the electrons heated by the laser interaction or Black Body radiation from large particles emitted by the target.
Figure 5.5: Emission within the wavelength region of 350-950 nm at 1 mm from the target for a fluence of 20 J/cm². Important to note is that this spectrum is not corrected for the wavelength dependent transmission of the grating and the quantum efficiency of the CCD array. The transmission is at least 5 times higher ~500 nm than at the long wavelength limit (900 nm).

The time integrated optical emission spectrum is dominated by emission features from the zinc atom, the zinc ion and the oxygen atom. No oxygen ion emission lines are observed. The emission is correlated, as in the case of the 193 nm graphite ablation, with third body recombination within the plume. The ions in the plume recombine with electrons to form preferentially highly excited products, i.e. highly excited Rydberg states. These highly excited Rydberg states radiatively cascade down to the ground state. The cascade down mechanism does not involve a preferential route so, in the emission spectrum, all of the more intense emission lines expected from these products are observed. The observed transitions of the zinc atom and ion are given in Figure 5.6 as Grotrian diagrams.
The proposal that three body recombination is the route for the observed emissions implies the existence of the reactant cation, thus observed Zn atom emission implies the existence of Zn$^+$ cations in the plume (observed), and that Zn$^{2+}$ ions are the source of the observed Zn$^+$ emission. The non-observation of oxygen cationic lines in the emission spectrum implies that the plume is not hot enough to support oxygen dications. In addition, the emission line list provided in reference 11 indicates that there are strong emissions arising from the O$^+$ cation in the observed wavelength region, supporting this statement. Comparing the ionisation potentials of the different observed species (9.39 eV for the zinc atom, 13.62 eV for the oxygen atom and 27.36 eV for the zinc cation) with the ionisation potential of the oxygen cation (48.74 eV) further supports this postulate.

Comparing the relative intensities of the emissions we see that the zinc cation lines have onsets at higher fluence and thereafter a steeper fluence dependence than the zinc atom lines. This is correlated with the creation mechanism of these ions. The observed optical emission is largely the result of the interaction of the laser photons with the ejected particles. This interaction can be divided into two processes, namely inverse Bremsstrahlung and multi-photon ionisation. The latter is generally considered to be more important in the case of UV laser ablation although, as has been shown in Chapter 4, MPI can trigger the inverse Bremsstrahlung mechanism (which is non-linearly dependent on the electron and ion concentration) by creating localised high concentrations of electrons and ions in the plume. The Zn $\rightarrow$ Zn$^+$ conversion can occur via a two-photon mechanism. Three 193 nm photons are necessary to create an oxygen
cation from a ground state O atom, which is a much less likely multi-photon absorption process. A more plausible explanation is that the O⁺ cations are created via laser-plume interactions induced by inverse Bremsstrahlung. The interaction will heat up the plume, and O⁺ ions can be created either by charge transfer via a high-energy collision between a zinc ion and an oxygen atom or via electron-neutral inverse Bremsstrahlung. Zn⁺ emission attributable to e⁺ Zn²⁺ recombinations, has a clear fluence threshold, which strongly indicates that these species are a secondary product of the ablation event arising from inverse Bremsstrahlung induced by the laser-plume interactions.

No plasma temperatures are calculated from the relative zinc atom to zinc cation emission since the intense zinc atom emission lines will be affected by self absorption, giving incorrect measures of their relative intensity and thus of the plasma temperature.

5.3.2. Time differentiated optical emission spectroscopy in vacuum

To gain information on the velocity of the emitting species the optical emission was also studied in time differentiated mode. The wavelength of an emission line is selected by a grating and the TOF transient is recorded by a PMT. The procedure gives species selective velocity information, as described in section 2.4.1. The emission lines selected for this study are 481.1 nm for the zinc atom, 776.9 nm for the oxygen atom and 491.4 nm for the zinc cation; TOF transients recorded for the different species are given in Figure 5.7 for three different distances.
Figure 5.7: TOF spectra of emissions monitored at 3, 6 and 9 mm from the target for (a) zinc atom (481.1 nm), (b) oxygen atom (776.9 nm) and (c) zinc cation (491.4 nm) lines. Note that the horizontal scale in (c) is five times smaller than in (a) and (b). All emission intensities are normalised to the same peak value.

The TOF transients illustrate that the velocity of the emitting zinc cations is higher than that of the emitting zinc and oxygen atoms. It is important to note that, the zinc cation emission will provide a measure of the $\text{Zn}^{2+}$ velocity distribution and that the neutral emissions reflect the motion of the respective cations, given the assumption that these emissive states are generated by third body recombination. In the further discussion we will assume that third body recombination is the general creation mechanism for these excited and radiatively decaying states ($\text{Zn}^+$ for neutral zinc atom emission, etc.). The TOF spectrum of the emitting zinc atoms (i.e. a probe of the nascent $\text{Zn}^+$ distribution) shows double peak behaviour, the early time part of which correlates with the observed $\text{O}$ emissions (and thus the nascent $\text{O}^+$ ions). The slow tail in the TOF spectrum is clearly evident at short distances (close to the target) but merges with the high velocity peak at later time scales. The double peak behaviour is most noticeable for the intense zinc atom lines (Figure 5.8), indicating that this is a universal
ablation behaviour correlated with all of the Zn emission lines. Interestingly, the zinc atom emission line with the least intense tail is the 636.4 nm line. This line also has the least intensity when recorded with the PMT and shows the lowest gradient on the Zn-ZnO correlation diagram (Figure 5.2).

![Figure 5.8: The TOF profiles of different Zn emission lines from ZnO ablation at 20 J/cm², measured 5 mm from the target surface.](image)

The 330.4, 334.5, 472.3 and 481.2 nm emission lines (a) show a bimodal distribution with a well distinguished slow tail, while the 636.4 nm emission line (b) shows a less pronounced bimodal distribution.

Further insight into the origin of the slow tail in the TOF spectrum of the Zn emission can be obtained by comparison with the TOF profile obtained for the oxygen emission, Figure 5.9. The slow tail observed for the TOF profile of the zinc emission lines is not noticeable in the TOF transient of the oxygen atom emission line. The TOF profile of the oxygen emission line appears to correlate with the fast part of the zinc emission TOF transient. This suggests that the ZnO ablation plume consists in fact of two separate distributions. The fast zinc distribution and oxygen distribution propagate at the same Centre of Mass (COM) velocity, which follows from hydrodynamic equilibration within the ZnO ablation plume, and a slower distribution is evident only in the zinc TOF profile. Secondly, this figure shows that the tail of the TOF profile of the zinc emission is less prevalent at later time scales and thus larger distances. This double peak could arise from photodissociation of molecular zinc fragments, e.g. Zn₂, though we consider this formation mechanism unlikely given of the high photon energy. Note that, for example no C₂ molecules were observed in 193 nm the ablation of graphite.
With this in mind, it is likely that ejection from the surface results in far more monatomic species than clusters; the photodissociation mechanism will thus be discarded in the following discussion. A more probable explanation for this behaviour will be presented later in this section.

![Graphs showing TOF signal versus distance for Zn^+ and O^+](image)

Figure 5.9: Comparison between the TOF of the 481.2 nm emission line of the zinc atom and the TOF of the 776.9 nm emission line of the oxygen atom at (a) 5 mm, (b) 9 mm and (c) 15 mm.

The velocity can be deconvoluted from these TOF transients by plotting the mean of the TOF signal versus the distance from the target surface at which the transient is recorded. Such plots are given in Figure 5.10, for the different recorded species. The zinc ion and the oxygen atom emission lines follow a linear distance versus time relationship, the gradients of which are correlated with the velocities of these species. The neutral zinc emission line has a more complicated distance versus time dependence, as expected from the observation of the double peak behaviour of the transient. The intercept with the y-axis is governed by the experimental error, since the viewing
column is ~2 mm in diameter; this error can be assumed to equate to ± 1 mm. The y-axis intercept of the fitted line to the points associated with the oxygen emission falls within this error bar (< 1 mm), but that for the line fitted to the points related with the Zn⁺ emission cuts the y-axis at ~3.5 mm, outside the acceptable error range. This large value for the intercept has been found in three separate experiments. A possible explanation for this behaviour is that the Zn⁺ cations are, during the onset of ablation, subjected to an initial acceleration, after which they propagate with a constant velocity. The offset is not important to the determination of a mean terminal velocity, since this is calculated from the gradient of the distance versus time plot.

The mean velocity of the emitting O atoms, for four different fluences, are given in Table 5.1, together with the calculated mean velocity of the emitting Zn⁺ ions at 20 J/cm². Thus the mean velocity for the nascent O⁺ and Zn²⁺ ions and the fast peak of the Zn⁺ distributions (monitored via O, Zn⁺ and Zn emissions, respectively) does not seem to depend greatly on the applied laser fluence. The kinetic energy corresponding to the O⁺ velocity distribution (monitored via O⁺ emission) is ~12 eV, for the fast peak of Zn⁺ distribution it is ~50 eV, while for the Zn²⁺ ions (monitored via Zn⁺⁺) it is ~305 eV. As Figure 5.10 shows, the zinc distribution appears to accelerate if one plots the local velocity (i.e. d/t) versus time.

![Figure 5.10: Mean distance versus time plot for different species at 20 J/cm². The lines through the plots for the emitting oxygen atoms and the zinc ions are least squares linear fits to the data points.](image-url)
<table>
<thead>
<tr>
<th>Monitored Species</th>
<th>Fluence (J/cm²)</th>
<th>Velocity (km/s)</th>
<th>Error (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O⁺</td>
<td>5</td>
<td>11.5</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12.5</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>12.9</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>12.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn⁺⁺</td>
<td>20</td>
<td>28.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 5.1: Mean velocities calculated for four different fluences for the monitored O⁺ species and for 20 J/cm² for the Zn⁺⁺ species. The reported error bar is the standard deviation of the calculated velocity observed for three separate sets of data.

A second way to analyse the data is to perform a Jacobian transformation and convert the TOF spectrum into velocity space. This procedure has been done for the emitting zinc atom, zinc ion and oxygen atom distribution and the resulting velocity distributions are given in Figure 5.11.

Figure 5.11: TOF-velocity conversion for nascent (a) Zn⁺, (b) O⁺ and (c) Zn⁺⁺ distributions from ZnO ablation at 20 J/cm². The transients for the emitting oxygen neutral and zinc cation distributions have been normalised to each other, while the transients for the emitting zinc neutral distribution are given unnormalised.
In velocity space the velocity distributions of the emitting Zn\textsuperscript{**} ions, the O\textsuperscript{*}, and the faster part of the distribution of Zn\textsuperscript{*} species are each independent of the distance at which the transient has been taken. This accords with the observation made for the TOF transients that the species propagate with a constant velocity. The velocity spread is also independent of the distance, giving a picture of a plume propagating with a constant COM velocity and velocity dispersion. From the converted TOF transients one can calculate a mean velocity and a velocity spread. This is given in Table 5.2 for the emitting oxygen atoms and the zinc ions.

<table>
<thead>
<tr>
<th>Monitored Species</th>
<th>Fluence (J/cm\textsuperscript{2})</th>
<th>Velocity (km/s)</th>
<th>FWHM (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsuperscript{*}</td>
<td>5</td>
<td>11.9 ± 0.1</td>
<td>9.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12.2 ± 0.7</td>
<td>9.9 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>12.8 ± 0.1</td>
<td>9.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>12.7 ± 0.2</td>
<td>9.8 ± 0.2</td>
</tr>
<tr>
<td>Zn\textsuperscript{**}</td>
<td>20</td>
<td>31.0 ± 0.1</td>
<td>9.2 ± 0.3</td>
</tr>
</tbody>
</table>

Table 5.2: Velocity and velocity spread of the emitting oxygen atoms and zinc ions as shown in Figure 5.11. The figures are obtained by fitting a split gaussian to the experimental distribution. For the emitting Zn\textsuperscript{**} ion distribution the slow tail was discarded in the process.

As can be concluded from Table 5.2 the oxygen cations (monitored via the O\textsuperscript{*} emission) propagate with a centre of mass velocity of ~12 km/s and a FWHM of ~10 km/s for all the fluences investigated. The zinc dication distribution propagates with a velocity of ~30 km/s with a FWHM of ~9 km/s. The ratio of the centre of mass velocity and the FWHM velocity spread is substantially smaller for the Zn\textsuperscript{2+} distribution than for the O\textsuperscript{*} distribution. This agrees with the picture that the zinc dications are localised towards the front edge of the ablation plume. In addition, the mean velocities obtained from the transients in velocity space are in close agreement with the velocities deduced from the raw TOF transients, validating the TOF-velocity conversion.

The slow tail of the zinc atom distribution exhibits an apparent acceleration, as can be derived from Figure 5.7. This apparent acceleration could have (at least) two origins. It could indicate a genuine acceleration of the zinc atom distribution, or it
could be an effect of the way the data are recorded. These TOF transients are a measure of the emitting species in the plume at different distances. Any depletion or decay process (e.g. radiative decay) will have more time to reduce the distribution of slow moving species before they reach the observation window; the 'mean' velocity of the observed distribution will thus appear to increase. This effect is also dependent on the distance of the viewing column, since the particles will need increasingly longer times to reach the viewing column with increasing distance. This will leave the slow species underdetected compared to the faster species and the discrepancy will increase with increasing distance.

To investigate the importance of either of the aforementioned effects, acceleration and decay, we have plotted the total signal recorded in different velocity bins for the different distances. We concentrate on measurements in the region of the slow velocity distribution (< 7 km/s). The results are shown in Figure 5.12.

![Figure 5.12: The total Zn⁺ emission signal in different velocity bins averaged over three different measurements for an applied laser fluence of 20 J/cm².](image)
The distance dependence of the signal in the different velocity bins does not follow the behaviour that might be expected from a radiative (or other) decay mechanism, namely an exponentially decaying function, rather we find that the total signal in the velocity bins peaks at a given distance before decaying. The total signal for higher velocity bins peaks at an increasing distance, consistent with a genuine acceleration of the slow distribution of emitting Zn* species.

This distribution, which we presume to reflect the nascent Zn+ distribution, will have to be deconvoluted. The method employed assumes that the zinc and oxygen cations have the same 'fast' velocity distributions, as illustrated by the TOF transients presented in Figure 5.9. If we assume that the velocity distributions are the same (within experimental error) we can deconvolute the total Zn* signal by simply subtracting a weighted transient resembling the O* distribution. The mean velocity of the resulting slow component of the Zn* distribution was calculated by finding the centre of the integrated signal, and the results verified by fitting a split gaussian to the distributions. The resulting velocity and the FWHM are plotted, as a function of distance, for four different fluences, in Figure 5.13. The acceleration obtained for the slow zinc ion distribution is relatively insensitive to the fluence; indeed the differences in acceleration derived for the different fluences are within the errors arising from the deconvolution procedure. Assuming a linear correlation between the mean velocity and time yields values in the range $5-10 \times 10^6 \text{ km/s}^2$ for the acceleration.
Figure 5.13: Velocity versus distance plots for the slow accelerating distribution prevalent in the zinc emission line at 481.2 nm, for four different incident fluences: a) 5 J/cm² b) 10 J/cm² c) 15 J/cm² and d) 20 J/cm². The dashed lines show the linear fit to the FWHM of the curves and the solid line is the linear fit through the experimentally determined COM velocities.

The implied velocity at the target surface (the y-intercept in Figure 5.13) and the velocities and the FWHM velocity spread at different distances are summarised in Table 5.3. The initial velocities scale with the fluence. These ejection velocities correlate with a surface temperature in the case of Knudsen layer formation, according to the following equation:\textsuperscript{12}

\[ kT_s = \frac{1}{\eta_K} \frac{mv^2}{2} \frac{T_s}{T_K} \]  

(5.1)

where \( k \) is the Boltzmann constant, \( \eta_K \) is a heat capacity dependent parameter, \( m \) is the mass of the particle (Zn), \( v \) is the velocity of the particle and \( T_s \) and \( T_K \) are the...
temperatures of the target surface and the Knudsen layer. The value of $|\eta K/T_0 T_s| (=2.52)$ can be calculated from thermodynamical parameters.\textsuperscript{12}

The calculated temperatures are 700 K for the fluence of 5 J/cm\textsuperscript{2} to 2200 K for the fluence of 20 J/cm\textsuperscript{2}. For comparison, the melting point of metallic zinc is 692 K. Thus the data are consistent with the idea that the zinc particles at low fluences are ejected from a zinc melt, which is heated up at higher fluences to a temperature near the critical point ($T_{c,Zn} = 3800$ K).\textsuperscript{20}

<table>
<thead>
<tr>
<th>Monitored Species</th>
<th>Fluence (J/cm\textsuperscript{2})</th>
<th>Velocity (m/s)</th>
<th>Velocity / Spread (m/s) at 5 mm</th>
<th>Velocity / Spread (m/s) at 10 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn*</td>
<td>5 J/cm\textsuperscript{2}</td>
<td>670 ± 240</td>
<td>3860 / 2450</td>
<td>7050 / 4250</td>
</tr>
<tr>
<td></td>
<td>10 J/cm\textsuperscript{2}</td>
<td>670 ± 110</td>
<td>3140 / 1900</td>
<td>5600 / 3050</td>
</tr>
<tr>
<td></td>
<td>15 J/cm\textsuperscript{2}</td>
<td>860 ± 90</td>
<td>3580 / 2130</td>
<td>6300 / 3500</td>
</tr>
<tr>
<td></td>
<td>20 J/cm\textsuperscript{2}</td>
<td>1180 ± 20</td>
<td>3130 / 1860</td>
<td>5080 / 2600</td>
</tr>
</tbody>
</table>

Table 5.3: Velocity and acceleration of the slow distribution of the zinc neutral emission according to the plots in Figure 5.13.

The detailed TOF analysis of the emissions accompanying the ablation plume arising from zinc oxide shows that the plume consists of three components namely a fast distribution attributable to Zn\textsuperscript{2+} ions in the plume, a slower component attributable to the O\textsuperscript{+} and Zn\textsuperscript{+} ions in the plume and a slow accelerating component apparent only in the Zn* emission that we also attribute to Zn\textsuperscript{+}. The data can be interpreted in the following way: The observed optical emission, in part at least, is a product of the interaction of the laser light with the ablation plume. The occurrence of fast Zn\textsuperscript{2+} ions (correlated with Zn\textsuperscript{+} emission) is consistent with the assumption of laser-plume interaction. The occurrence of an O\textsuperscript{+} and Zn\textsuperscript{+} distribution (correlated with O and Zn emissions, respectively), with similar COM velocities, indicates a hydrodynamic, velocity-equilibrating regime. Both distributions are assumed to be emitted by the zinc oxide lattice.

A second distribution, associated only with slower Zn\textsuperscript{+} ions, shows accelerating behaviour that can be attributed to an electrodynamic effect in the plume. The calculated ejection velocities suggest that these ions are ejected by a melt of metallic
zinc. This reflects the way the experiment is carried out, i.e. the ablation emanates from a pre-ablated track, which is enriched in zinc, as will be reported in section 5.3.4. The results are in accordance with an earlier TOF-mass spectrometer study of ZnO ablation with KrF laser excitation at fluences in between 0.4 and 2.5 J/cm². This study also identified plume splitting and acceleration, for the Zn⁺ distribution only. The obtained results were discussed in the framework of Coulomb explosion and will be discussed further in section 5.3.6.

The acceleration of at least a part of the plume has interesting consequences and will be investigated further by an independent measurement, namely Langmuir and ion probes.

5.3.3. Langmuir Probe transients in vacuum

The plasma was additionally studied with Langmuir/ion probes. The probe voltages were set to +10-20 V to ensure that the probe is operating in the electron acceleration region. The transient electron density was studied at distances of 3 - 9 cm from the target surface and at fluences of 5-20 J/cm². Typical currents, summed over 30 laser shots, with the probes biased at different voltages to ground at 3 cm from the target for a fluence of 10 J/cm² are given in Figure 5.14.
Figure 5.14: Probe currents at different voltages recorded with a delay on the oscilloscope of 1 \( \mu \text{s} \), measured at 3 cm from the target surface and a fluence of 10 J/cm\(^2\). The spike at 1 \( \mu \text{s} \) is correlated with signal arising from scattered light of the target hitting the probe and inducing a current via the photoelectric effect, it shows the onset of the laser-material interaction.

Clearly at these voltages, the ion current does not have the same shape transient as the electron current. The ion current is dependent not only on the amount of ions in the plasma but also on the electron temperature, as shown in Chapter 2. The electron temperature is higher in the high velocity part of the plume, as indicated by the presence of Zn\(^{2+}\) ions in this region. This also implies that the ion current is overestimated in the front part of the plume, which is a possible explanation for the differences in the measured probe currents. Additionally the ion current at lower applied voltages shows a double peak, reflecting the behaviour correlated with the electrons. The measured electron current is assumed to be in the electron acceleration regime. This assumption is verified by plotting the square of the electron current versus the probe potential for 20 different voltages in the range of 10 - 20 V, and calculating the square of the correlation.
coefficient ($R^2$) of the obtained curve. This is shown in Figure 5.15 and the interpretation of such measurements is discussed in detail in reference 13.

![Figure 5.15](image)

Figure 5.15: (b) Electron currents at different probe voltages in the range of 10-20 V as also shown in Figure 5.14 and (a) the time dependence of the $R^2$ value calculated assuming a linear voltage-(current)$^2$ relationship.

Figure 5.15 indicates an excellent linear relationship between the square of the probe current and the voltage in the region where the probe current is measurable above the noise level. The region with the smallest correlation coefficient is the rising edge of the current plot, possibly reflecting shot-to-shot variations in the fluence and the target surface.

The electron current was studied in this way for eight different fluences and the measured TOF converted into velocity space. A number of the original TOF distributions and their corresponding velocity distributions are given in Figure 5.16. The mean velocity and the FWHM can be calculated from these converted velocity distributions. The figures are given in Table 5.4.

The calculated mean velocities and the FWHM’s scale with the applied fluence, though the increase in velocity is small compared to the increase of applied fluence.
Noticeable in the TOF and velocity distributions is the existence of a small peak correlated with a fast electron distribution. This fast electron distribution travels ~45 km/s and is apparent in all the measured transients. These deduced velocities can be compared with the data obtained via OES, although care has to be taken in the comparison since the techniques measure inherently different quantities. With OES, the transient behaviour of a radiative decaying transition of a selected atom or ion is measured close to the target, while the Langmuir probe reveals the transient behaviour of the total electron density at larger distances from the target. The mean velocities measured with the Langmuir probes closely resemble those measured for the emitting zinc and oxygen atoms (which we associate with nascent Zn\(^+\) and O\(^+\) ions), while the velocity of the fast electron distribution resembles that measured for the Zn\(^+\) emission (i.e. the nascent Zn\(^{2+}\) ions). The mean velocities measured with the Langmuir probe assembly are higher than the mean velocities deduced via optical emission spectroscopy and their FWHM are smaller. Overall, the Langmuir probe transients show a rather complex behaviour, correlated with the ablation of multi-component species. The Langmuir probe transients are assumed to consist of (at least) three contributions. The electron distribution comprises a component that is loosely coupled (via ambipolar diffusion) with the expanding Zn\(^{2+}\) ions, another coupled with the expanding Zn\(^+\) and O\(^+\) distribution and, presumably, a third slow component loosely coupled with the expanding slow Zn\(^+\) distribution. Because of this complexity, no deconvolution has been performed on these data. Important to note is that the relative height of the fast peak in the TOF distribution increases with increasing fluence consistent with the noted fluence dependence of the Zn\(^{+}\) emission (and thus the Zn\(^{2+}\) formation). A comparison with a study for a monocomponent material (Al, given in appendix 1) can be made.
Figure 5.16: (a) TOF and (b) velocity distributions for electrons measured at four different fluences at 3 cm from the target surface. The TOF profiles are all recorded so that \( t=0 \) (i.e. the instant when the laser is incident on the target) appears at 1.0 \( \mu \text{s} \).

<table>
<thead>
<tr>
<th>Fluence (J/cm(^2))</th>
<th>Velocity (km/s)</th>
<th>FWHM (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>13.3 ± 0.2</td>
<td>4.5 ± 0.1</td>
</tr>
<tr>
<td>7.5</td>
<td>14.3 ± 0.7</td>
<td>5.1 ± 0.6</td>
</tr>
<tr>
<td>10</td>
<td>15.8 ± 0.1</td>
<td>5.9 ± 0.1</td>
</tr>
<tr>
<td>12.5</td>
<td>17.1 ± 0.5</td>
<td>7.1 ± 0.6</td>
</tr>
<tr>
<td>15</td>
<td>16.7 ± 0.5</td>
<td>6.4 ± 0.9</td>
</tr>
<tr>
<td>17.5</td>
<td>17.8 ± 0.3</td>
<td>7.4 ± 0.3</td>
</tr>
<tr>
<td>20</td>
<td>18.3 ± 0.6</td>
<td>8.1 ± 0.8</td>
</tr>
</tbody>
</table>

Table 5.4: Mean velocity and FWHM of the electrons (deduced from the centre of the integrated distribution) at different recorded fluences and with the probe-target distance of 3 cm. The error bars represent the standard deviation of at least three independent measurements.

This apparent plume splitting into two, or more, components has also been noted in the ablation in vacuum of copper\(^{13,14}\), iron\(^ {14}\) and graphite\(^ {15}\) at similar fluences and distances to our work and a short discussion of plume acceleration observed in the case of aluminium ablation is also given in appendix 1. The explanation provided for this behaviour is based on the existence of fast, hot electrons in the plume. The mechanism
for creation of these fast electrons involves laser-plume interactions. The laser photons can heat up the electron distribution directly, via inverse Bremsstrahlung. Hot electrons situated at the front of the plume can escape the plasma plume, due to the lack of energy equilibrating collisions. This causes a high positive potential, which in turn accelerates ions in the plume to higher energy. These ions will rapidly reach the same average velocity as the electrons. Because of the low collision rate the ion and electron clouds will actually oscillate through each other's position. After the interaction the forward velocity of the ion and electron cloud should ultimately become equal.

The acceleration of a part of the ablation plume has been identified via TOF-OES at small distances from the target surface. To investigate the extent of any acceleration at larger distances from the target surface we have performed electron probe measurements at different distances for a given fluence of 20 J/cm². The results are summarised in Figure 5.17.

![Figure 5.17](image)

Figure 5.17: (a) A plot of the mean electron velocity versus distance for a fluence of 20 J/cm² together with (b) various of the corresponding Langmuir probe measurements at four different distances, 3 cm, 4 cm, 5 cm and 6 cm at the given fluence. The four plots in (b) are on a common vertical scale.

The whole electron distribution accelerates, as can be derived from Figure 5.17. The mean velocity versus distance plot indicates that the acceleration gradually dies out at distances > 7 cm from the target. Figure 5.17 also illustrates that the total signal does not attenuate significantly with increasing distances. This has also been described in other studies investigating double layers in ablation plumes. The observation has been
attributed to a self-focusing effect of the electron/ion distribution apparent in accelerating ablation plumes, which results in a highly forward-peaked distribution for the ions/electrons.\textsuperscript{14} Alternatively, however, we note that it could also be due to the increased Debye length at larger distance and thus lower number densities. The validity of either of these effects will have to be checked by future studies involving an angular dependent study or time gated OES with a CCD-camera. Also noticeable is that the FWHM of the electron distribution is not greatly affected by the acceleration. To study the dependence of the acceleration on the fluence we have also studied the distance dependence of the mean velocity at a number of different fluences. The results are summarised in Figure 5.18.

![Figure 5.18](image.png)

**Figure 5.18:** Acceleration of the plume given at different probe distances: 3, 7 and 9 cm. The dashed line shows a third order polynomial fit through the data for 3 cm.

The acceleration and the asymptotic velocity scales with the fluence, as expected. The higher the laser power input, the higher the fraction of fast electrons and the higher the mean electron velocity. The acceleration over the range of 3 to 7 cm is around 20\% for the lowest fluence, increasing to \~ 40\% at the highest fluence studied. The fluence increase induces an increment of the fraction of Zn\textsuperscript{2+} ions and fast electrons, giving the incline in the mean electron velocity by changing the ratio of the fast (coupled with Zn\textsuperscript{2+}) and slower electrons.
The analysis of the plume with Langmuir probes reinforces the conclusions of the OES study that, at least, a part of the plasma component of the plume is accelerating due to a fast, decoupled electron component. The fast electron distribution is observable with the Langmuir probe transients and its velocity is ~45 km/s. The electron distribution within the plume accelerates even at distances of 3 – 7 cm from the target surface, although the acceleration is much less pronounced than the acceleration observed closer to the target surface. This observation is in accord with the assumption that this acceleration has an electrodynamic origin. The almost negligible signal attenuation observed when measuring at increasing distances can be attributed to either a self-focusing effect within the plume or a compensation effect whereby the reduced number density at larger distances is offset by the increase in Debye length.

Combination of the TOF-OES and Langmuir probe studies shows that the nascent Zn\(^+\) distribution and, at least at later times, the total electron (and thus ion) distribution accelerates under the influence of an electric field in the plasma generated by laser-plume interactions. This behaviour appears to be quite general for ablation of metals at high fluence (5-20 J/cm\(^2\)) and even graphite (at higher fluences: 10-25 J/cm\(^2\)). A discussion of the ablation behaviour of aluminium under the same conditions, included in appendix 1, serves to confirm these results.

5.3.4. Target morphology

The surface of the ZnO target changes drastically under the influence of laser irradiation. The irradiated part of the white-yellowish target surface becomes grey after a single laser shot, in accordance with observations reported in reference 10. This is an indication of a non-congruent evaporation mechanism during ablation leaving the target surface zinc enriched. Figure 5.19(a) shows a low magnification picture of the ZnO surface after laser ablation. Three regions are distinguishable in this figure, namely the region modified directly by the laser irradiation, a second region characterised by an indirect surface modification and the third, the apparently unaffected, region of the target surface.
Figure 5.19: SEM pictures of the zinc oxide surface (a) low resolution image of the zinc oxide target surface, the ablation region is indicated by the arrow, (b) higher resolution image of the boundary between the ablated and heat affected zone (horizontal bar = 20 µm), (c)-(d) higher resolution images of non ablated and the ablated areas, respectively.

In higher detail (Figure 5.19(b)-(c)-(d)) the unaffected region exhibits a crystalline structure with clearly distinguishable crystal facets, while the indirectly modified region exhibits a smoother structure with evidence of resputtered droplets on the surface. The surface structure of the laser irradiated region has a very smooth appearance. These observations can be explained as follows: The laser irradiation induces local heating, melting and ablation not only of the directly irradiated region, but also of the neighbouring region both via heat conduction in the solid target and by interaction with the lower intensity edges of the incident laser pulse. The irradiated region is ~400 µm wide, consistent with the focused laser beam width, the heat conduction affected zone extends for a further ~100 µm. Figure 5.19(d) suggests that the depth profile of the ablated region includes regions with differing conductivity, as indicated by the different greyness of the two regions.

In addition, the composition of the surface was analysed by X-Ray microanalysis and gives the figures shown in Table 5.5. The X-Ray microanalysis system is calibrated...
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with a virgin target surface, which is assumed to comprise 1:1 stoichiometry. The analysis was performed with 20 keV electrons, the penetration depth for this kinetic energy is highly material dependent, but an often-stated value for the penetration depth for crystalline solids is ~1 μm. The figures indicate a high zinc enrichment in the ablation track and the heat affected zone, and the figures are in agreement with the SEM pictures. This surface layer is thus assumed to consist of highly zinc enriched ZnO or a metallic zinc layer on top of the zinc oxide lattice.

The figures for the surface stoichiometry also indicate some zinc enrichment far from the ablation track. This is assumed to be attributable to redeposition of zinc droplets on the target surface.

<table>
<thead>
<tr>
<th></th>
<th>Zn %</th>
<th>O %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin target</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Unablated Area</td>
<td>59.9</td>
<td>40.1</td>
</tr>
<tr>
<td>Indirect surface modification</td>
<td>64.5</td>
<td>35.4</td>
</tr>
<tr>
<td>Ablated area</td>
<td>66.0</td>
<td>34.0</td>
</tr>
</tbody>
</table>

Table 5.5: X-Ray microanalysis figures of the Zinc and oxygen content in the films.

The removal rate was calculated from mass loss studies and yielding values of 0.13 μg/shot for 5 J/cm² and 0.31 μg/shot for 20 J/cm². This gives an ablation rate of ~1 - 5 × 10¹⁵ atoms/shot and, assuming a density of 5.675 g/cm³ and a spot size of 0.4 ×1 mm², implies a crater depth of ~ 60 - 300 nm /shot.

5.3.5. Optical emission and ion probe measurements in background gas

The plume properties in a small background pressure of O₂ were investigated at a fluence of 10 J/cm² by TOF measurement of the 776.9 nm O⁺ emission at small distances from the target surface (< 15 mm) and, additionally, at distances comparable with the deposition distance (5 cm) via Langmuir probes. The time integrated wavelength dispersed spectrum in these low background pressures of O₂ showed no significant differences from the spectrum obtained in vacuum.
The TOF-OES distributions for three different distances from the target surface are shown in Figure 5.20 with the corresponding distance versus time plot at a background gas pressure of 10 mTorr. The mean velocities deduced from the TOF profiles can be compared with the velocities deduced for ZnO ablation in vacuum and indicate that the emitting O\(^*\) component of the plume propagates in 10 mTorr of background O\(_2\) with a comparable velocity to that in vacuum. Comparing the total emission intensity versus the distance (Figure 5.20) shows that the total signal drops significantly faster in the presence of added background gas than in vacuum. The quenching of the total signal can be explained as follows: The excited oxygen distribution in a small background pressure will decay radiatively, by emission of a photon, or non-radiatively, by collisional energy transfer to another atom/molecule (most probably the background gas). Those oxygen atoms that collide with the background gas molecules have less chance of being observed in optical emission. These atoms are also the ones that are most likely to transfer momentum to the background gas. That the O\(^*\) emission shows the same propagation velocity in 10 mTorr O\(_2\) as vacuum may well reflect the fact that the observed emitting atoms in both cases are those that have managed to avoid collision prior to emitting. The fact that the forward directionality of the ablation plume is little affected by addition of small amounts of background gas at distances < 5 cm has been recognised in earlier studies, and is reviewed in reference 17.
Figure 5.20: (a) TOF-OES emission spectra of O\textsuperscript{*} emission at 776.9 nm for 10 J/cm\textsuperscript{2} and 10 mTorr O\textsubscript{2} background pressure (1 \mu s delay on the oscilloscope), (b) distance versus time plot compared with the data in vacuum. (c) Total signal versus distance plot for the O\textsuperscript{*} emission following ablation 10 J/cm\textsuperscript{2} of ZnO in vacuum and in a background pressure of 10 mTorr O\textsubscript{2}. The curves in (c) are first order exponential curves (of the form $y = y_0 + A e^{-\frac{x}{\lambda}}$), the value of the exponential factor $\lambda$ was 2.3 in the case of vacuum ablation and 1.6 in the case of ablation in 10 mTorr, quantifying the faster decay of the emission in background gas compared to vacuum.

The ablation plume was also studied with Langmuir probes as described earlier, as a function of added O\textsubscript{2} pressure. The TOF transients and velocity converted profiles for the electrons are given in Figure 5.21. These transients were recorded successively, at different O\textsubscript{2} pressures, under otherwise identical experimental conditions. Two effects are observable, namely an increase in electron current with increasing O\textsubscript{2} pressure and a complicated redistribution of the velocity distribution with part slowing and part increasing in velocity.
The increase in electron current when ablating in a background gas indicates ionisation of the background gas molecules. This ionisation occurs when the high kinetic energy atoms, arising from the ablation event, collide with the background gas molecules. The mean kinetic energies derived in vacuum for the Zn ions are 50 eV for the Zn\(^+\) ions (measured by Zn\(^*\) emission) and 305 eV for the Zn\(^{2+}\) ions (measured by Zn\(^{2+*}\) emission). These kinetic energies are more than sufficient to obtain the observed additional ionisation of the background gas (total electron density ~ 2 times larger than in vacuum). The fast end of the electron distribution, associated with the Zn\(^{2+}\) ions, appears to grow in importance with increasing pressures of O\(_2\), but the mean velocity decreases. The slow part of the electron distribution propagates with similar mean velocity, but the FWHM of this part of the distribution increases substantially with addition of background gas. This is attributable to the well-known 'snow-plough' effect of the ablation plume.\(^{18}\) While propagating through a background gas, the ablation plume pushes the background molecules forward, thus giving a forward velocity to the background gas. The FWHM of the total ion signal is expected to increase as a consequence of this effect.

![Graph showing signal transients over time and velocity for different pressures.](image)

**Figure 5.21:** Langmuir probe transients of electrons in the plume resulting from 193 nm ablation of ZnO in a background pressure of O\(_2\) recorded at a distance of 3 cm.
5.3.6. Conclusions from studies of the 193 nm pulsed laser ablation of zinc oxide

The ablation of zinc oxide has been studied in vacuum and small pressures of O₂ background gas. Existence of zinc cations and dications and oxygen cations in the ablation plume has been inferred from studies of the time integrated optical emission. These ionic products are considered to be generated largely, if not exclusively, by laser-plume interactions. The intensities of the zinc and oxygen atom emissions depend linearly on the applied laser fluence while the zinc ion emission depends non-linearly on the laser fluence and shows an apparent threshold of ~ 10 J/cm².

Time differentiated OES shows that the ablation plume can be divided into (at least) three components, a fast Zn²⁺ ion component, a component correlated with the congruent formation of Zn⁺ and O⁺ ions and a component correlated only with the formation of slow Zn⁺ ions. The latter component is deduced to be accelerating as it evolves away from the target. This acceleration behaviour is confirmed with the Langmuir probe assembly. The acceleration scales with the applied fluence and has ceased by distances ~7 cm. Such behaviour was also noted and discussed ¹⁰ in an earlier TOF-mass spectrometer study of ZnO ablation in vacuum with 248 nm laser excitation at fluences between 0.4 to 2.5 J/cm². The zinc atom distribution observed in this earlier work at low fluences (0.4 - 0.7 J/cm²) showed an increasing kinetic energy from 1 to 4 eV with increasing fluence; these energies were attributed to an electronic ejection mechanism. The zinc ion distribution was seen to exhibit double peak behaviour at fluences above 0.7 J/cm², which was identified as the plasma formation threshold. This double peak behaviour was attributed to the existence of Zn²⁺ ions in the plume ejected by lattice defects (doubly ionised F-centres). These Zn²⁺ ions could, in turn, recombine to form Rydberg states which would be detected as emitting Zn⁺ ions. The ejection of Zn²⁺ ions is also considered to cause acceleration of the plasma via a Coulomb explosion mechanism followed by charge transfer and neutralisation. The existence of Rydberg states in the ablation plume was inferred by comparison of the kinetic energy distributions of the detected Zn⁺ and Zn²⁺ ions and, additionally, by photoionisation using the output of a pulsed frequency doubled YAG laser operating at 0.25 J/cm²: as here, their formation was attributed to third body recombination in the
plume. The behaviour of these Rydberg states was comparable with the behaviour of the parent ion.

When comparing the two sets of results it is important to note that we work at a higher photon energy and higher fluences, and that we specifically sample the decaying Rydberg states with OES and the total ion distribution with the Langmuir Probes. The observation that the Rydberg atoms show basically the same behaviour and velocity as their parent ion validates our assumption of treating the emitting states as probes for the respective parent ions. In our study we observe analogous double peak behaviour, although in our OES studies we are specifically probing radiating states derived from the Rydberg states. Since our study is in a higher fluence region, we assume that, because of laser-plume interaction, some species originally formed in the ground state will have undergone photoionisation, recombination, Rydberg formation and subsequent optical emission. Our results suggest that the ejection mechanism for the accelerating zinc ion distribution is more related to ejection from a zinc melt rather than electronic ejection from defect sites in the ZnO lattice. Additionally, the whole plume undergoes an acceleration due to electrodynamic effects in the plume: this we tend to attribute to a development of a double layer at the expanding front of the plume, associated with fast, hot electrons rather than a Coulomb explosion mechanism.

The difference in fluence employed in the two studies may be a contributing factor for the differences in proposed ion ejection mechanism. Applying a high fluence will obviously have a more devastating effect on the target surface composition, and conceivably, would increase the zinc enrichment. Indeed, there will likely be a fluence threshold where the dominant ejection mechanism switches from ejection from defect sites in the ZnO lattice, to ejection from a zinc melt.

Detailed analysis of the post ablated area reveals that the target surface is zinc enriched and that the ablation track has a surface layer of zinc enriched zinc oxide or metallic zinc on top of the zinc oxide lattice. The zinc enriched surface is created either by preferential oxygen ejection or by Zn redeposition.

The velocity of the emitting species in the ablation plume is not significantly affected by the introduction of small pressures of oxygen background gas (5-10 mTorr). A TOF-OES study of the oxygen emission shows no deceleration of the emitting oxygen atoms within the plume, although comparison of the signal intensity versus distance decay rate in O2 and in vacuum ablation suggest that atoms which undergo collisions, and thus might be decelerated, are also quenched and thus no longer...
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contribute to the observed emission. The LP studies reveal that the electron density in the ablation plume is ~ 2 times higher when ablating in a small background pressure of oxygen, indicating additional ionisation of the background gas molecules. The fast end of the electron distribution (correlated with the Zn\(^{2+}\) ions) is slowed (35 km/s as compared with 55 km/s in vacuum). Because of the mass of the Zn atoms, this part of the plume has a huge kinetic energy (in vacuum = 305 eV) and can easily ionise the background gas molecules via momentum transfer. The slower part of the electron distribution is seen to be much broader in a background pressure compared with in vacuum. This is attributable to the 'snow-plough' effect observed in laser ablation, where the ablation plume transfers part of its forward momentum to the background gas and sweeps it in front of the plume of ablated material.

5.4. Pulsed laser deposition of zinc oxide and properties of the resulting films

Zinc oxide deposition was studied in vacuum and in small background pressures of oxygen gas (0 - 10 mTorr) over the temperature range of RT – 500 °C. The influence of the different ablation parameters on the resulting film properties was studied. A laser fluence of 10 J/cm\(^2\) was chosen for all of these studies. The films were analysed by UV-VIS absorption spectrometry, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Photo-Luminescence (PL) and Laser Raman spectrometry. Films were deposited on quartz and on silicon.

5.4.1. Dependence of parameters on deposition conditions and film properties

The dependence of the film properties on the ablation parameters can be investigated by use of XRD, planar TEM, UV-VIS absorption, PL, Raman Spectroscopy, AFM and SEM. XRD provides macroscopic information, while planar TEM gives microscopic information, about the crystal structure. UV-VIS absorption
and PL provide information about the electronic structure of the deposited films while Raman spectroscopy gives a picture of the phonon modes in the film material. SEM and AFM reveal details of the surface structure of the films. All films are grown for 15 minutes (9000 laser shots) unless stated otherwise.

5.4.1.1. UV-VIS

The UV-VIS spectra of the deposited films under different growth conditions are given in Figure 5.22. The influence of the background gas, the substrate temperature and the effect of post annealing have been studied.

Figure 5.22: UV-VIS spectra of ZnO films deposited under different conditions: (a) the dependence on the background pressure and the temperature, (b) the dependence on different background gases O₂ and N₂, films grown at a substrate temperature of 500 °C and 10 mTorr of background gas and (c) the dependence on post-deposition annealing (5 hours / 800 °C / air), original film grown at room temperature in vacuum. The step observed in (a) is an artefact created by switching lamps in the UV-VIS spectrometer.
As Figure 5.22 illustrates, the UV-VIS absorption is very dependent on the background pressure. Films deposited in vacuum have a significant, continuous absorption in the visible range, demonstrating the presence of a considerable amount of metallic zinc in the deposited films grown under these conditions. The metallic zinc can be incorporated in the film as droplets or as domains of metallic zinc co-deposited with zinc oxide. The increase in transmission at energies above the band gap of films grown at higher temperature, but still in vacuum, is likely to be related, in part, to a decrease in film thickness. The introduction of background gas improves the film quality greatly. Films deposited in a low pressure of background O$_2$, at various temperatures, show no decrease in absorption at energies above the band gap (Figure 5.22(a)). This suggests that the film thickness does not decrease as in the case of vacuum deposition, but that any metallic Zn within the films largely oxidises in the presence of the background O$_2$. To have a better understanding of the influence of the background gas, we compared deposition in a background gas of oxygen and nitrogen under the same conditions. The background gas can affect the film properties in two ways. First, it can reduce the amount of droplets incorporated in the film, by retarding the particulates ejected from the target. If the pressure is high enough, these particulates do not reach the target surface.¹⁹ It will be illustrated in the SEM results (section 5.4.1.2) that the particle density in the films is substantially reduced when depositing in a background pressure. A second effect of the background gas is to react with material in the ablation plume and/or with the deposited film. Obviously, in the present case we only anticipate any such reactions with added O$_2$. The absorption results given in Figure 5.22(b) suggest a convolution of the two effects; N$_2$ addition does improve the film quality, but there is still some continuum absorption at energies below the band gap. The absorption at frequencies above the band gap also indicates that the films grown in an N$_2$ atmosphere are thinner than those grown in O$_2$. The ZnO band gap is observable as a sharp feature at ~3.4 eV in the absorption spectrum of the highest quality films (400-500 °C / 10 mTorr O$_2$) and the transmission in the visible region is >90 %.

The effect of post ablation annealing in air at 800 °C for 5 hours of a film originally deposited at room temperature (RT) and under high vacuum has been studied also (Figure 5.22(c)). The post-annealed film shows a much improved UV-VIS absorption. This post ablation annealing process indicates that the films can absorb O$_2$ post-
deposition (at high temperatures) to reduce the defects in the lattice. This indicates that the films are thin and porous enough to absorb oxygen at the grain boundaries - these being assumed to be the preferential location of the visible light absorbing defects.

5.4.1.2. SEM

The deposited films have also been analysed by SEM imaging. Images of films grown under different deposition conditions are shown in Figure 5.23. The films deposited in vacuum are smooth on a ten nanometer scale, but show a large number of embedded particulates. These particulates are a side product of the explosive boiling process at the target surface and deposit on the substrate with high kinetic energies.20

The number of particulates is reduced greatly by introducing a background pressure. This is in accordance with the idea that the large particulates will be slowed sufficiently in a background pressure not to be deposited.19

Deposition at elevated substrate temperatures leads to hollows in the deposited films. The hollows are assumed to be remnant craters caused by impacting large particulates. Presumably high substrate temperatures either encourage evaporation of the large particulates \( (T_m \text{ of Zn} = 692.7 \text{ K} / 419.5 \text{ °C} ) \) or the release of temporally accommodated particulates as a result of pressure build up by trapped gas pockets.
Films deposited at higher temperatures also show surface cracks. These cracks are presumed to arise during the cooling of the substrate, as a result of stresses in the film induced by a difference in thermal expansion coefficient of the substrate and the deposited film.

The film thickness was analysed by cross sectional SEM; representative images are shown in Figure 5.24. The films, deposited for 15 minutes, (9000 shots) have a thickness of ~ 200 nm, the high temperature deposited films show the same cracks as observed in the planar SEM pictures.
5.4.1.3. XRD

The crystallinity of the films was studied via XRD and TEM. XRD spectra of several films grown in vacuum at different temperatures are given in Figure 5.25(a). This figure clearly shows that the films exhibit preferential alignment at a substrate temperature of 400 °C. The main crystal growth axis is the (002) axis, with its ideal peak position at 17.263°, in good accord with the figures provided by other studies of laser deposition of ZnO.21 No other XRD peaks attributable to ZnO are apparent in the spectra.

The effects of post-annealing and variation in background pressure were also studied and the results are shown in Figure 5.25 (b), and (c) - (d) respectively. At elevated temperatures, there is a large difference between the XRD spectra of films deposited in background pressure and in vacuum. Preferential alignment occurs in background pressures. The shift of the peak position is assumed to be related to the stoichiometry of the films. Films with a large deviation from the 1:1 stoichiometry have smaller (002) diffraction peak intensities. The stoichiometry and crystallinity of the films improves with higher O₂ pressures, showing a shift towards the theoretical (002) value.
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Figure 5.25: Selected XRD measurements for ZnO films grown under different deposition conditions. (a) deposition with 10 mTorr O\textsubscript{2} background gas at given temperatures, (b) 2 films deposited at 400 °C / 10 mTorr, one film not annealed (Unann) and the other film annealed for 5 hours at 800 °C in air (Ann), (c) and (d) pressure dependence of the film quality at 200 °C and 400 °C, respectively. The diffraction angle associated with an ideal (002) surface is given as a dashed grey line.

The effect of post annealing is shown in Figure 5.25(b). Post annealing improves the film alignment only when the starting material is already aligned. This observation is in accord with the assumption that badly aligned films will need to undergo a bulk relaxation to obtain the preferential alignment. Post-deposition annealing at temperatures below the melting point of ZnO ($T_m = 1974.8$ °C \cite{22}) does not provide a route for total bulk relaxation and reorientation.
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Figure 5.26: XRD spectra illustrating the effect of substrate: (a) and (c) ZnO films deposited on silicon and quartz, together with their respective rocking curves (b) and (d). The curves through the data points in (b) and (d) are Gaussian fits and yield FWHM values of 1° for (b) and 2° for (d).

The effect of substrate has been studied also, by depositing films on quartz and silicon. The results are given in Figure 5.26. These indicate that the substrate composition and the lattice mismatch are actually of minor importance for depositing a c-axis aligned film. The rocking curve shows a broader gaussian for films grown on quartz than on silicon, but, in both cases, the dominant growth axis is the (002) axis.

5.4.1.4. Planar TEM

The preparation of the films for the TEM studies reported here will be discussed in some detail. Given the high kinetic energies of the impacting particles, it is impossible to use a standard copper TEM grid with a thin DLC film (~10 nm) deposited above the voids of the grid. Rather than depositing on the DLC films, the ablated particles actually break it down. Thus, a different approach has been investigated in which a thin
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film is deposited on top of a DLC film deposited on mica. Since mica expands when inserted in water, the DLC film lifts off the mica surface and can be used as the substrate for planar TEM analysis. The same procedure without a DLC layer on top was tried also, but did not produce a free-standing ZnO film.

Since TEM can only be applied to intrinsically thin substrates the films were deposited for 2 minutes and at two different deposition temperatures, RT and 400 °C with 10 mTorr of O₂ background gas. The film thickness can be estimated from the cross sectional SEM results (Figure 5.24) yielding a value ~15 nm. Figure 5.27 shows selected planar Bright Field TEM figures of the films together with their Selected Area Diffraction (SAD) patterns. The TEM images show a nanostructured film with single crystal sizes of 5 - 10 nm. This observation is in accordance with earlier reported results.²³ The SAD patterns, of selected parts of the film, investigated with the same magnification, have been arranged to have similar image intensities (by changing the exposure time of the camera). Comparison of the SAD patterns of the deposited films reveals that the diffraction ring related to (002) and (100) diffraction in the film deposited at RT disappears in the film deposited at 400 °C. This correlates with the observations from the XRD measurements that the films deposited at higher temperatures show a higher amount of structuring. The Bright Field images in Figure 5.27 show clearly that the RT grown film displays far less crystallinity than the film grown at 400 °C; this is in accordance with the XRD results. Note that the RT deposited film shows a large hole on the Bright Field picture, this is assumed to be an artefact in the film, the edges of the hole were actually used to focus on the surface.
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Figure 5.27: Selected Bright Field TEM figures of the deposited films at (a) RT and (b) 400 °C together with their respective SAD patterns. The indices of the lattice diffractions are given for the SAD patterns.

Additional analysis can be performed by calculating the lattice spacing from higher resolution images by taking cuts through the diffraction patterns, as shown in Figure 5.28. The prominent diffraction fringes show separations of 2.81 Å and 2.46 Å, associated with the (100) and (101) crystal directions, respectively. No diffraction
fringes with $d = 2.61$ Å, correspond to the (002) lattice spacing, were distinguishable, indicating that the (002) lattice direction is a minority in-plane growth lattice direction. Important to note also is that the images taken for the film grown at low temperatures do not exhibit a fully crystalline character. Although some crystalline domains are observable in the images, most of the image area consists of highly disordered material, from which it is not possible to produce a diffraction pattern.

![Figure 5.28: Higher resolution TEM image showing a crystalline domain in the 400 °C film. Two cross sectional intensity plots obtained from the images, (a) one for the (101) crystal direction and (b) one for the (100) crystal direction.](image)

The planar TEM and XRD images cannot be compared straightforwardly. They are complementary, planar TEM images yield information about the in-plane structure of the films, while the XRD data reveals the structure of the surface plane. The apparent
lack of diffraction fringes correlated with the (002) lattice direction in the plane indicates that the (002) lattice direction is the prominent surface plane. The majority of the surface of films grown at RT shows a disordered or amorphous structure, in accordance with the observed lack of any peak in the XRD measurements. The measurements are in good accordance with TEM results from one recent study \(^ {23}\) although the SAD patterns in the former work seem to be saturated thus providing less quantitative information about the differences in lattice structure under different growth conditions.

5.4.1.5. AFM

AFM measurements of the surface topography of the ZnO film grown under the 400 °C, 10 mTorr O\(_2\) growth conditions are shown in Figure 5.29. The films appear to exhibit significant roughness, showing a variation in height of \(\sim\)30 nm. The phase profile, obtained by tapping mode AFM, shows the presence of columnar structures \(\sim\)50 nm in diameter, this columnar growth is also discussed in reference 23 and is correlated with the \(c\)-axis aligned growth.
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5.4.1.6. Raman and Photoluminescence

The Raman and PL spectra of ZnO films were recorded at the 325 nm He-Cd-laser excitation wavelength. Since this laser excitation wavelength is close to the band gap (350 nm) the spectra provide data on the UV resonant Raman scattering in the ZnO lattice.24,25 The resulting Raman spectra are given in Figure 5.30. The spectra are dominated by the LO (longitudinal) mode at 580 cm\(^{-1}\), of \(E_1\) symmetry, of a c-axis aligned ZnO crystal and its overtones (1165 and 1749 cm\(^{-1}\)). These spectra are typical for c-axis aligned crystals. In monocrystalline samples as many as 7 overtones have been recorded.24 In the present ZnO films produced by laser ablation up to 3 overtones have been observed although the third overtone is barely distinguishable because of the strong band gap luminescent behaviour of these films. There is, to our knowledge, no

Figure 5.29: AFM images of the same area on a ZnO film grown under 400 °C, 10 mTorr O\(_2\) growth conditions, (a) height profile and (b) phase profile.

The AFM images indicate a highly porous film which exhibits a columnar growth. The porosity of the film indicates that the films are nanocrystalline and suggest that many grain boundaries exist in the films. This picture accords with the figures obtained from the planar TEM images (Figure 5.27) and with the cross-sectional SEM images (Figure 5.24), both of which show surface structure of the order of tens of nanometers.
prior information about resonant Raman spectroscopy on laser ablated thin films of ZnO. The Raman spectrum seems to be dependent on the quality of the film, poorer quality films exhibit weaker overtone signals.

![Figure 5.30: Raman spectra for films deposited under different conditions, (a) vacuum / RT, (b) 10 mTorr O₂ / RT, (c) vacuum / 400 °C and (d) 10 mTorr O₂ / 400 °C.](image)

Photoluminescence at room temperature was also studied following excitation at a wavelength of 325 nm. The results are shown in Figure 5.31. The spectra show an intense feature around 380 nm associated with band gap luminescence. The photoluminescence behaviour is highly dependent on the film quality. All four spectra are recorded with the same microscope and spectrometer settings, and the total luminescent signal for the different films is not normalised. The results show that the film deposited at 400 °C / 10 mTorr O₂ exhibits the most intense and also the sharpest 380 nm luminescence while films deposited at lower temperatures and in the absence of background gas exhibit a weaker, broader luminescence peak related with band gap states. A second photoluminescent feature that is most pronounced in the high quality film is the broad luminescence centred around 510 nm. This green photoluminescence
is related with band emission from deep interband levels, which are identified as either oxygen vacancies or zinc interstitials.\textsuperscript{26,27}

5.4.2. Effect of Aluminium and Gallium doping

The effect of aluminium and gallium doping was investigated by ablating sintered pellets of zinc oxide mixed with 5% aluminium or gallium. XRD spectra of films deposited at $500 \degree C / 10$ mTorr $O_2$ are given in Figure 5.32, while the UV-VIS spectra of films deposited under the same conditions are given in Figure 5.33.
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Figure 5.32: Comparison between XRD spectra of films grown by ablating targets comprising 5% (a) aluminium and (b) gallium dopants in ZnO at 10 mTorr background pressure of O₂ and at 500 °C. The vertical scaling is equal for both of the figures. The intense peak at ~69° is a reflection from the Si(100) substrate.

The displayed XRD spectra show the 2θ angle in contrast with the former XRD figures. The peak at 34.4° agrees with the (002)-alignment of ZnO while the feature at 69.3° is a reflection of the Si(001) substrate. Interestingly, the XRD spectrum of the aluminium-doped film indicates a much less (002)-aligned film than the gallium-doped film. The reason for this observation might be that significant dopant concentration can affect the lattice structure in the film. Simply from size considerations, one might suspect a higher lattice distortion due to incorporation of the much smaller Al³⁺ ion (compared with Zn²⁺) than a Ga³⁺ ion. This will be discussed in more detail in section 5.5.4.
Figure 5.33: UV-VIS spectra of gallium doped ZnO film and a pure ZnO film deposited under the same conditions.

The optical band gap is little affected by the dopant concentration as illustrated in Figure 5.33. Doping with Ga, if anything, seems to shift the absorption edge to slightly higher energy. Both of the deposited films are ~ 90 % transparent in the visible region.

5.4.3. Conclusions and discussion of the deposition of ZnO films

The quality of the deposited film is highly dependent on the deposition conditions. Optimal deposition conditions for ZnO are 400 °C/500 °C and 10 mTorr of O₂ background gas. The background gas not only prevents deposition of large droplets in the film, but also contributes to achieving more stoichiometric film formation (as shown by comparing the UV-VIS absorption spectra of films deposited in O₂ and N₂ background gas). Temperature is the most important parameter for film alignment. As discussed in reference 17, the substrate temperature necessary for lattice relaxation is ~0.3 Tm which, in the case of ZnO, is 592 °C (Tm = 1974.8 °C 22). Once again, we see
that the high kinetic energy of the ablated particles allows deposition of highly aligned films at substantially lower temperatures than 0.3 \( T_m \).

The studies of deposition on different substrates shows that c-axis aligned or (002) growth is actually not dependent on the substrate morphology. This shows that the growth is not epitaxially defined but that the (002) surface is thermodynamically the most stable growth surface. The reason for the stability of the (002) surface is still to be determined (see section 5.5). Previous theoretical modelling suggests that the (100) surface should actually be the most stable surface and that a significant fraction should rearrange as the polar (001) and \((00\overline{1})\) phase.\(^{28}\)

The surface structure is also highly dependent on the deposition conditions. Deposition in vacuum yields films with a large density of droplets or particulates, which are assumed to be created on the target surface as zinc droplets. These particulates can be largely eliminated by growing in a background gas, whereby gas dynamic effects cause retardation and stopping of these large particulates before they reach the substrate surface. Films grown on high temperature substrates show two kinds of defect structures; hollows and cracks. The hollows are assumed to be remnant impact craters of large particulates. The high temperatures either cause the large particulates to evaporate (\(T_m\) of Zn = 692.7 K / 419.5 °C) or are presumed to release the particulates because of pressure build up by trapped gas pockets. The cracks arise from the different temperature dependent expansion coefficients of the substrate and the deposited film. AFM revealed that the surface of the films grown under 400 °C/10 mTorr \(\text{O}_2\) conditions have a roughness of \(\sim 30\) nm, exhibit columnar growth and are nanocrystalline (\(-\)tens of nanometers). This picture is consistent with TEM and high resolution SEM results.

The resonant Raman spectra show the LO phonon mode of the (002) surface and its overtones for films grown under all conditions, but the relative intensity of the different overtones is dependent on the film quality. The photoluminescence signal is very dependent on the deposition conditions, with the film grown under optimal conditions (400 °C/10 mTorr \(\text{O}_2\)) showing green luminescence from zinc interstitials/oxygen defects as well as strong 380 nm band gap luminescence.

Doping the films with aluminium or gallium has been attempted using mixed Al:ZnO and Ga:ZnO pellets with 5% concentration of dopant. The (002) peak in the XRD spectrum of the aluminium-doped film almost disappears under growth conditions similar to those used to grow a highly aligned pure ZnO film, whereas this peak prevails.
in the gallium-doped film. This observation will be discussed in section 5.5.4. Ga doping has little effect on the optical band gap of the ZnO lattice, as shown via UV-VIS absorption spectroscopy.

5.5. *Ab initio* calculations

The crystal structure of ZnO was studied via plane wave, periodic HF and DFT calculations with the CRYSTAL98 (version 1.0) code.\(^ {29} \) The basis set used was a purpose built double-\( \zeta \) basis set for solid state calculations of the ZnO structure.\(^ {30} \) The gradient corrected DFT calculations were performed with the Becke 3-parameter functional approach (B3LYP), the Becke88 functional was used for the Exchange functional and the Lee-Yang-Parr functional was used for the Correlation functional.

5.5.1. Bulk structure of the wurtzite structure

The crystal bulk structure was optimised by locating the relative O and Zn atomic positions at the wurtzite lattice positions, and then independently varying the \( c \)- and \( a \)-values of the unit cell of the hexagonal wurtzite structure using Hartree Fock (HF) and Density Functional Theory (DFT) levels of theory. The energy surfaces so obtained are given in Figure 5.34. The calculated values for the HF and DFT optimised bulk structures are given in Table 5.6.

![Energy surfaces for the bulk geometry optimisations via (a) HF and (b) DFT calculations.](image)
### Table 5.6: Comparison of the optimised parameters obtained in the present work using HF and DFT calculations with the results of other theoretical calculations and with experimental values for the lattice parameters $a$ and $c$. The third column shows the ratio $c/a$. The fourth and the fifth column indicate the percentage difference from the experimental values, the sixth column reports the calculated absolute Mulliken charges on the atoms and the last column gives the calculated total energy of the systems in Hartree.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$a$ (%)</th>
<th>$c$ (%)</th>
<th>Charge ($e$)</th>
<th>Energy (Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>3.285</td>
<td>5.245</td>
<td>1.597</td>
<td>-1.31</td>
<td>-0.97</td>
<td>1.62</td>
<td>-3705.430480</td>
</tr>
<tr>
<td>DFT</td>
<td>3.310</td>
<td>5.190</td>
<td>1.568</td>
<td>-2.08</td>
<td>0.09</td>
<td>1.36</td>
<td>-3709.098675</td>
</tr>
<tr>
<td>Ref. 31</td>
<td>3.259</td>
<td>5.183</td>
<td>1.590</td>
<td>-0.51</td>
<td>0.23</td>
<td>-</td>
<td>-3705.426610</td>
</tr>
<tr>
<td>Exp.</td>
<td>3.243</td>
<td>5.195</td>
<td>1.602</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-3705.426610</td>
</tr>
</tbody>
</table>

Comparing the figures given in Table 5.6 shows that the calculated parameters agree with experiment to within an acceptable (~2 %) errors, although the HF optimised geometry has the $c/a$ ratio closest to the experimental values. The calculated parameters are also in good agreement with values reported from former HF ab initio calculations.\(^\text{31}\) The basis set in our calculations is of better quality than that used in reference 31, as indicated by the total energy.

The Mulliken charges on the zinc and oxygen atoms show that the lattice has significant covalent character, manifesting itself by the large deviations in the charges from the ionic values (i.e. ± 2 $e$). Additionally, we note that inclusion of the effect of electron correlation (via the DFT theory) has a large impact on the atomic charges and makes the lattice even less ionic than predicted by the HF results.

The surface and doped structures reported hereafter have been calculated with the HF optimised lattice parameters since these parameters are in closest agreement with the experimental ($a$, $c$ and $c/a$) values. Calculations were performed at both the HF and DFT level of theory, unless stated otherwise.
5.5.2. The non-polar (100) surface

The non-polar surfaces are the most straightforward to calculate and results of calculations on these surfaces have been reported previously.\textsuperscript{28,32} We have calculated the energy of the non-relaxed non-polar (100) surface as a function of slab thickness. The results are summarised in Figure 5.35. The surface energy is found to be 1.48 J/m\textsuperscript{2} for the unrelaxed surface.

![Figure 5.35: (a) Surface energy as a function of the slab thickness, and (b) stacking sequence of (100) surface. The big spheres represent Zn and the small sphere O.](image)

The (100) surface has also been investigated at the DFT level of theory,\textsuperscript{32} with relaxation taken into account. The relaxations for this surface are generally quite small and involve a modest contraction of the bond length (0.1 Å) of the surface ZnO dimeric units and a small buckling of the surface layer, which induces a tilt in the surface dimeric (ZnO) unit of 5° (the oxygen relaxes outwards and the zinc inwards). No surface energy was reported in this study.

5.5.3. The polar (002) surface

The most common surface structure obtained with laser ablation, as seen in section 5.4.1.3, is the polar (002) surface. Theoretical calculations on this surface could provide key information about the formation and the properties of these c-axis aligned
films. Unrelaxed polar surfaces are inherently unstable, as discussed in Chapter 3. The surface will have to relax via a change in surface charge (charge transfer) to compensate for the overall dipole moment, or via a reconstruction that renders the surface defective. In apparent contradiction to such ideas, however, a recent computational study of this polar surface has reported an energy minimum involving only relatively small geometry relaxations.

In this paragraph we will discuss the results of our HF/DFT calculations within the framework of these other theoretical studies. To gain a better view of the relaxation, we have calculated small slabs (2,4 bilayers) and optimised their geometry. The ZnO lattice has two different terminations, namely the oxygen terminated (001) surface and the zinc terminated (001) surface. The picture of the relaxation of these two surfaces is even more complicated, since these surfaces are inherently different and so will relax in different ways. Theoretically, it is impossible to calculate a surface energy for just one of these surfaces, since both the surfaces have to be taken into account.

5.5.3.1. Two-bilayer slab

The two-bilayer slab is characterised by the lack of bulk (or non-surface) layers to support the surface structure. Although this is, of course, not a physical model to describe the surface structure of nanometer thick ZnO films, a discussion of the calculations is given because it provides a simple introduction to the fundamentals of this polar surface.

A representation of the two-bilayer slab is given in Figure 5.36. The first approach to relaxing the structure involves moving the position of both of the outer layers or both of the inner layers along the c-axis relative to the bulk position and calculating the properties of these geometric arrangements. In this way we can study the effect of dipole moment on the energy and the electronic structure. The second approach to relaxing the structure is to optimise the system by independently displacing the four layers, where only geometry conserving displacements are allowed (along the c-axis). The distance between the Zn and O layer in each bilayer is 0.6 Å. We have investigated the displacements in which the outer layers are moved from 0 to -0.3 Å (inward relaxation) and inner layers moved from 0 to 0.3 Å (outward relaxation) relative to their...
bulk position. Clearly, such a movement of 0.3 Å (in absolute value) of both of the outer and inner layers relative to their bulk position leads to a planar structure.

![Diagram of two-bilayer slab and geometrical parameters](image)

Figure 5.36: (a) Representation of the two-bilayer slab and (b) the geometrical parameters for the bulk like structure, moving the inner layers 0.3 Å and the outer layers – 0.3 Å results in the planar geometry. The big spheres represent Zn and the small sphere O.

We have investigated the energy dependence on the former type of displacement, given in Figure 5.37. The minimum in this 2-parameter space is the planar geometry. This is also the only calculated geometry that does not exhibit a dipole moment. The plots show that the dipole moment has a very large effect on the energy. The relative energy difference between the two extremes, the planar structure and the bulk structure, of the computational grid is 0.1347 Hartree for the HF and 0.08502 Hartree for the DFT calculations. The relative DFT energy difference is about half the relative energy difference calculated at the HF level of theory, indicating that electron correlation plays an important part in the description of the electronic structure of this system.
Figure 5.37: Energy versus nuclear displacement for the 2-bilayer slab. The outer layer axis defines the absolute displacement of the outer layer, while the inner layer axis defines the absolute displacement of the inner layer in Å. The geometry where the x- and y-values are 0.0 corresponds with the bulk structure while the geometry with 0.3 for x- and y-values corresponds with the planar structure. The x- and y-axis are the displacement of the inner and outer layer, respectively, and the z-axis shows the energy of a given geometry, at (a) HF and (b) DFT level of theory. 'Inner' signifies displacement of the inner layers while 'Outer' signifies displacement of the outer layers.

The change in electronic structure has been investigated by calculating the Mulliken charges on the atoms. These Mulliken charges provide an estimate of the charge density and the changes in charge density induced by the displacements. The calculated charges on the atoms in the extreme cases of a fully planar geometry and an unrelaxed bulk geometry are given in Table 5.7. In the further discussion we introduce parameters that can be calculated from the Mulliken charge distribution. The charges on the atoms can be multiplied by the positions of the atoms and summed to yield a value for the dipole moment. The charge transfer between one bilayer and the other can be calculated by summing the charges on the atoms in each bilayer, and an average value for the covalency can be estimated by summing the charges on one species (e.g. the zinc atoms) and divide this charge by the number of atoms in the computational cell, here two. The smaller the resulting charge, the more covalent the lattice is. A value of ±2 indicates an ionic solution, while a value of 0 indicates a totally covalent solution.
Table 5.7: Charges on the atoms (in units of $e$) for the two extremes of the calculation, the fully planar geometry and the geometry of the unrelaxed bulk structure.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Zn outer</th>
<th>O Inner</th>
<th>Zn Inner</th>
<th>O Outer</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar</td>
<td>1.56</td>
<td>-1.56</td>
<td>1.56</td>
<td>-1.56</td>
</tr>
<tr>
<td>Bulk</td>
<td>1.35</td>
<td>-1.49</td>
<td>1.45</td>
<td>-1.31</td>
</tr>
<tr>
<td>DFT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar</td>
<td>1.36</td>
<td>-1.36</td>
<td>1.36</td>
<td>-1.36</td>
</tr>
<tr>
<td>Bulk</td>
<td>1.14</td>
<td>-1.33</td>
<td>1.27</td>
<td>-1.08</td>
</tr>
</tbody>
</table>

The charges on the atoms (and correspondingly their covalent character) are, for all bar one case, smaller than in the bulk calculations (given in Table 5.6). The exception is the case of planar co-ordination, at the DFT level of theory, where the calculated charges are the same as their bulk values. In addition, the non-planar solutions to the calculations show a charge transfer. The outer Zn atom becomes less positive (correlating with partial filling of the outer valence Zn band) and the outer oxygen atom becomes less negative (which correlates to partial depletion in the outer valence O band). This charge transfer corresponds to an induced dipole moment counteracting the dipole moment associated with the bulk polar surface. Interestingly, the induced dipole moment serves to make the bonds also more covalent. The charge transfer between the oxygen terminated $(00\bar{1})$ and the zinc terminated $(001)$ surface is $|0.14|\ e$ in the HF calculations and $|0.19|\ e$ for the DFT calculations. The charge transfer between the two layers is correlated with the displacement of the layers, as given in Figure 5.38.

Figure 5.38: Plots of the charge transfer between the two bilayers as a function of nuclear displacement calculated at (a) HF and (b) DFT levels of theory. 'Inner' signifies displacement of the inner layers while 'Outer' signifies displacement of the outer layers.
The total charge transfer is mainly associated with charge transfer between the oxygen atoms. The charge difference between the inner and outer oxygen atoms (\(|0.13| e\)) is almost twice the value of the difference between the zinc atoms (\(|0.07| e\)) derived using DFT theory. Since the charges are calculated as a function of displacement (a computational parameter) we can also calculate the dipole moment along the c-axis from the Mulliken charges. The results are given in Figure 5.39.

![Figure 5.39: c-axis dipole moment for the 2-bilayer slab as predicted from (a) the HF and (b) DFT calculations. 'Inner' signifies displacement of the inner layers while 'Outer' signifies displacement of the outer layers.](image)

Figure 5.39: c-axis dipole moment for the 2-bilayer slab as predicted from (a) the HF and (b) DFT calculations. 'Inner' signifies displacement of the inner layers while 'Outer' signifies displacement of the outer layers.

The calculated dipole moment is larger in the HF than in the DFT calculations, indicating that electron correlation helps to compensate for the original dipole moment arising from the polarity of the surface. This is also evident from the calculated charge transfer between the layers (Figure 5.38) and the energy of the polar solutions. Larger charge transfer is predicted by the DFT calculations, while the energy of the polar solutions is lower compared to the non-polar solution.

In addition, the geometry was optimised (energy minimised) in a 4-parameter space, namely the z-coordinates of the atoms of the four layers. The obtained values for the energy and electronic properties can be studied in this 4-parameter space to obtain a more general view of the way properties depend on each other. The calculated dipole moment can also be compared with that for the structures that would be predicted in the limit that there was no electronic relaxation, this latter dipole moment can be calculated from the product of the bulk charges (\(\pm 1.36 e\)) and the respective positions of the atoms. The two values have been calculated for all of the geometries investigated in
this section and plotted against each other (Figure 5.40(a)). The correlation between the two values can be fitted well by a second order polynomial. This result might be considered surprising at first sight, since the correlation appears to hold for any calculated geometry. This implies that the induced dipole moment at any specific geometry (or set of nuclear positions) is related with the dipole moment it would have prior to relaxing the original wavefunction irrespective of the specific geometry. The second order relationship indicates that the induced dipole moment gains in importance as the dipole associated with the unrelaxed wavefunction becomes greater. In the upper limit of the calculations, the dipole moment of the relaxed wavefunction is 54% that of the dipole moment of the unrelaxed wavefunction. The correlations between the dipole moment associated with the relaxed wavefunction and the associated charge transfer and measure of covalency are given in Figure 5.40(b)-(c). As expected, the dipole moment correlates with the charge transfer, but the system also becomes more covalent because of the dipole moment.

Figure 5.40: (a) Plot of the relaxed dipole moment versus the theoretical dipole moment for an unrelaxed wavefunction. (b) and (c) show the correlation between the charge transfer, and the covalency, with the dipole moment of the relaxed wavefunction.
The correlation of the calculated energy of the system with these various defined parameters can also be studied. The dependence of the energy on the charges on the individual atoms is given in Figure 5.41. Clearly, the energy is most closely correlated with the charges on the outer Zn and O layers.

Figure 5.41: Dependence of energy on the charge on individual atoms. 'Outer' and 'Inner' defines an atoms in the outer and inner layers, respectively.

The energy dependence of the defined electronic parameters is shown in Figure 5.42. The energy increases with increasing dipole moment and (in absolute values) charge transfer. This indicates that it is energetically unfavourable to have surfaces with a large polarity, as stated previously, although the wavefunction tries to counteract the polarity by a charge transfer giving rise to an induced dipole moment. The energy rises with higher covalent character of the atoms. Surprisingly, we observe that the lattice can sustain a small dipole moment, resulting in a calculated energy minimum, which is not totally planar. The structure is resembles the planar structure except for the inner Zn layer, which has an inner displacement of 0.09 Å.
5.5.3.2. Four-bilayer slab

The four-bilayer slab was also investigated theoretically. This structure is the smallest slab that has a unit cell as a bulk layer as Figure 5.43 shows (for an unrelaxed structure). For the four-bilayer slab the surface structure of the two surface bilayers (001 oxygen terminated and 001 zinc terminated surface) was optimised while the structure of the two inner bilayers was held fixed at the geometry of the bulk structure.

The optimised geometrical parameters and the associated relative energies of the four-bilayer slab are given in Table 5.8. In addition, the energy of the total planar geometry (inner and outer layers) was calculated for comparison with results presented in the former section.
Table 5.8: Structural parameters for the relaxed surface structure and relative energy compared with the total planar geometry. Minus sign indicates inward relaxation and 0.3 Å is the displacement corresponding to the planar structure.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) Zn layer</td>
<td>-0.28 Å</td>
</tr>
<tr>
<td>(001) O layer</td>
<td>+0.30 Å</td>
</tr>
<tr>
<td>(001) Zn layer</td>
<td>+0.17 Å</td>
</tr>
<tr>
<td>(001) O layer</td>
<td>-0.25 Å</td>
</tr>
<tr>
<td>Energy</td>
<td>$6.36 \times 10^{-2}$ Hartree</td>
</tr>
</tbody>
</table>

Figure 5.43: Structure of the four-bilayer slab. The big spheres represent Zn and the small sphere O.

The calculated energy of the structure with relaxed surfaces but with the inner two bilayers set to the bulk geometry is higher than that of the totally planar structure, indicating that the relaxation of the surfaces will involve not only reconstruction of the surface layers, but also relaxation of layers deeper in the bulk. Next to that, geometry in which the structure of the two inner bilayers was set to the bulk structure shows a high degree of surface relaxation. This relaxation is more pronounced on the (001) zinc
terminated surface than the (00\overline{1}) oxygen terminated surface. Consistent with this, DFT optimisation of a seven bilayer slab, reported in reference 33, without bulk relaxation, yielded values for the interlayer spacing of 0.14 Å for the Zn terminated (001) outer bilayer and 0.25 Å for the O terminated (00\overline{1}) outer bilayer. The results from the present relaxation studies cannot be compared easily with those obtained for relaxation of the two-bilayer slab. The four-bilayer slab has an inherent bulk dipole moment which is absent in the planar two-bilayer calculation. This bulk dipole moment induces a smaller geometrical relaxation of the surface bilayers and the positions of these bilayers are thus closer to the bulk values.

Figure 5.44 addresses the question whether the surface relaxation is governed solely by the dipole moment. Clearly the calculated energy minimum is not the structure with lowest dipole moment, indicating that the energy of this system is not governed just by the dipole moment.

Figure 5.44: Energy versus dipole moment for the four bilayer slab.

Again the calculated dipole moment can be plotted against the theoretical dipole moment associated with the unrelaxed wavefunction. The results are given in Figure 5.45. The correlation indicates that the charge transfer reduces the total dipole moment in the lattice by \sim \text{70 \%}, which is much higher than in the two-bilayer case, and indicates that introducing an intervening bulk structure enhances the stability of the dipolar
solution. Charge transfer between the surfaces, and change in covalency, is only a minor effect in this system as can be deduced from Figure 5.45(b) and (c).

Figure 5.45: (a) Dipole moment of the relaxed wavefunction, (b) charge transfer and (c) covalency plotted against the dipole moment associated with the unrelaxed wavefunction.

The calculations on the two- and four-bilayer slabs indicate that surface relaxation in the dipolar ZnO surface occurs towards a less polar surface than a bulk terminated surface. The calculated minimal energy surface in the case of the two-bilayer slab is nevertheless not the non-polar, planar surface. Comparing the energies of the unrelaxed four-bilayer slab with the totally planar one indicates that relaxation of the (001)/(001) surfaces will relax not only the outer surface layers but will also stretch deeper in the bulk. A second possible surface relaxation route is reconstruction. In the next section, we therefore consider a $2 \times 2$ reconstruction.
5.5.3.3. $2 \times 2$ reconstruction

A $2 \times 2$ reconstruction is another route for reducing the dipole moment. We have considered the reconstruction involving creation of a defective surface by removing $\frac{1}{4}$ of the oxygen and the zinc atoms from the outer layer. As shown in Chapter 3, this reconstructed surface should have an overall dipole moment of ~0 Debye. Only the structure with the bulk geometrical parameters was investigated, without any structural relaxation. The slab thickness was chosen to be 8 bilayers and the calculation was performed at the HF level of theory. A representation of the structure is given in Figure 5.46, and shows a structure with holes in the surface layer.

![Figure 5.46: Structure of a reconstructed geometry, with bulk geometrical parameters and $2 \times 2$ surface reconstruction as described in the text.](image)

The charges on the atoms, calculated via a Mulliken population analysis, are given in Table 5.9. The charges on the zinc and oxygen atoms in the first two layers of the defective zinc surface are also given in the table as $O_1$ and $Zn_1$. The charges on the zinc and oxygen atoms on the defective oxygen surface are given as $O_2$ and $Zn_2$. The charge transfer between the zinc and oxygen terminated surface was calculated as $-0.05 \, e$ (zinc surface more negatively charged than oxygen surface) and the dipole moment equates
1.45 e.Å. Compared with the values (0.5 to 0.9 e.Å) for the dipole moment of the unreconstructed four-bilayer slab this value is slightly higher although this might be attributable to the difference in level of theory (the calculations for the four-bilayer slab are at DFT level of theory). Interestingly, the theoretical value of the dipole moment for this amount of bilayers with the unreconstructed surfaces and the charges taken as the bulk charges equates 15.5 e.Å. This shows that the surface relaxation via reconstruction is definitely a viable route for diminishing the dipole moment.

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>-1.57</td>
<td>1.58</td>
</tr>
<tr>
<td>O₁ / Zn₁</td>
<td>-1.45</td>
<td>1.41</td>
</tr>
<tr>
<td>O₂ / Zn₂</td>
<td>-1.42</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Table 5.9: Values of the atomic charge (in units of e) obtained from the Mulliken population analysis for the calculations on the defective surface. 1 represents the Zn terminated surface and 2 stands for the oxygen-terminated surface.

It has to be noted that the number of layers included in the calculation is still quite small and that, for a more valid analysis, the number of layers considered should be increased. Calculations should be performed also at the DFT level of theory, given the importance of electron correlation in the structures described previously.

### 5.5.4. Effect of bulk doping: Aluminium and Gallium

The effect of doping was investigated by replacing a Zn atom in in a $2 \times 2 \times 1$ supercell by an Aluminium or Gallium atom. These limited dimensions were chosen because of computational restrictions. The structure of the supercell is given in Figure 5.46 and the atom labels are used in the further discussion.
The calculations were performed only at the HF level of theory, assuming a uniform background electron density to cancel the charge induced in the lattice. The dimensions of the unit cell were set to the Hartree-Fock optimised values, and the positions of the dopant neighbouring oxygen atoms were optimised. The neighbouring oxygen atoms were divided into two groups during this optimisation, reflecting the symmetry of the system. The neighbouring oxygen atom with the bond along the c-axis was treated independently from the three other oxygen atoms (see Figure 5.46). The geometry optimisation yielded the result that the oxygen atoms were drawn closer to the aluminium or gallium atom as shown in Table 5.9.

<table>
<thead>
<tr>
<th></th>
<th>O10</th>
<th>O13, O14, O16</th>
<th>Energy difference (Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.25</td>
<td>0.20</td>
<td>-5.96 x 10^2</td>
</tr>
<tr>
<td>Ga</td>
<td>0.15</td>
<td>0.10</td>
<td>-2.61 x 10^2</td>
</tr>
</tbody>
</table>

Table 5.9: Displacement of the oxygen atoms from their bulk values (as shown in Figure 5.46) in Å and the energy difference between the relaxed and unrelaxed geometries.
The contraction of the bond lengths to the oxygen atoms around aluminium is substantially higher than to the oxygen atoms around gallium, reflecting the relative sizes of the dopant atoms. The energy difference upon contraction is twice as high for aluminium as for gallium. The Mulliken charges have also been calculated from the electron density. Their values are summarised in Table 5.10.

<table>
<thead>
<tr>
<th></th>
<th>Al:ZnO</th>
<th>Ga:ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al /Ga</td>
<td>2.17</td>
<td>1.74</td>
</tr>
<tr>
<td>Zn</td>
<td>1.61</td>
<td>1.61</td>
</tr>
<tr>
<td>O (nb)</td>
<td>1.45</td>
<td>1.56</td>
</tr>
<tr>
<td>O</td>
<td>1.56</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Table 5.10: Mulliken charges for the different atoms, in e. O(nb) stands for the average value on the neighbouring atoms, while the average charge on non-neighbouring atoms is presented in O.

The Mulliken charge for the gallium atom is much lower than that for the aluminium atom, providing evidence for a much more ionic bond to O in the case of Al compared to Ga. In the case of Al, the charges on the neighbouring oxygen atoms are also affected, while in the case of gallium the neighbouring oxygen atoms have the bulk Mulliken charge.

5.5.5. Conclusion regarding the ZnO doping from the *ab initio* calculations

The effects of bulk doping have been considered theoretically, and Al and Ga doping has been compared. The neighbouring oxygen atoms around the aluminium dopant show larger relaxations than in the case of gallium doping; these observations correlate with a higher energy difference between the relaxed and unrelaxed structure. In addition, the aluminium-oxygen bonds show higher ionicity than the gallium-oxygen bonds. The high relaxation of the bulk structure associated with aluminium doping might indicate that the dopant prefers to be situated on the surface, although more detailed modelling of the effect of dopant atoms on the surface structure would be
necessary to prove this point. High concentrations of Al dopant would be predicted to disrupt the crystal structure, consistent with the XRD spectra.

5.6. General Conclusion

In this chapter we have tried to present a coherent and general overview of the pulsed laser ablation and deposition of ZnO and the structure of the deposited films. Interesting aspects of both the behaviour of the ablation plume and the characteristics of the resulting film have been highlighted.

The ablation plume has an inherent multicomponent behaviour. The velocity of at least one part of the plume, correlated with Zn$^+$ ions, exhibits an accelerating behaviour. We suggest that these zinc ions are created from a surface layer of molten metallic zinc.

The properties of the deposited films are highly dependent on the deposition conditions. Good quality films are deposited on substrates maintained at high ambient temperatures (400 °C) and in the presence of a low pressure (10 mTorr) of O$_2$ background gas. The films can be doped with gallium and aluminium, but the aluminium doped films deposited even under these optimal conditions show considerable disorder indicating that aluminium disrupts the lattice. The optical band gap appears to be little affected by the doping.

Theoretical calculations highlights the importance of surface relaxation for these films, since unrelaxed (001)/ (00\overline{1}) surfaces are inherently unstable. A first approach to a valid ab initio description of this surface is reported.

5.7. References

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6. Imaging of ablation plumes from KrF ablation

6. Optical Emission Spectroscopy and imaging of ablation plumes following ultraviolet KrF nanosecond, picosecond and femtosecond excitation of graphite in vacuum.

6.1. Introduction

The nanosecond KrF laser ablation of graphite is a well-studied subject; as in ArF laser ablation the process is mainly used for production of thin films of Diamond like Carbon (DLC)\(^1\) and Carbon Nitride (CN) films.\(^2\) The characteristics of the deposited films are crucially dependent on the properties of the ablation plume i.e. the degree of ionisation and the velocity of the species contained within the plume. Because of this, the plume characteristics have been extensively studied by means of Mass spectrometry\(^3\), Optical Emission Spectroscopy\(^4\)\(^-\)\(^6\), Ion probe measurements\(^7\)\(^-\)\(^10\) and Intensified Charge Coupled Device (i-CCD) camera imaging\(^1\)\(^,\)\(^11\).

The subject of pico- and femtosecond KrF laser ablation, as opposed to nanosecond ablation, has received much less attention. Femtosecond laser pulses have been applied to grow Diamond-like Carbon\(^12\) and Carbon Nitride films\(^13\), but there is a very little information concerning the composition of the plume under these specific ablation conditions. The closest studies to compare with are the following: The work of Qian et al.\(^12\) which provides a systematic ion probe investigation of the ablation plume following 100 fs titanium-sapphire laser irradiation. The study of Shirk et al.\(^14\) supplies information about the properties of the irradiated spot on the target surface under 120 fs - 20 ps titanium-sapphire laser irradiation. Rode et al.\(^15\) studied the plume properties with optical emission spectroscopy for a 60 ps Nd:YAG laser system.

This chapter presents results of a comparative study of laser ablation of graphite with nanosecond (25 ns), picosecond (5 ps) and femtosecond (450 fs) Krypton Fluoride (\(\lambda = 248\) nm) laser pulses. The techniques used in this study are Optical Emission Spectroscopy (OES) and i-CCD imaging of the plume. These techniques enable us to
study qualitatively the degrees of ionisation in the ablation plumes and quantitatively the velocity distributions of emitting species contained within the plume.

The degree of ionisation is inferred by interpretation of emission spectra of the various ablation plumes. The spectrometer used to disperse this emission into its constituent wavelengths operates in time integrated and time gated mode within a wavelength range of 360 - 900 nm.

Time gated images of the ablation plume are obtained by i-CCD imaging. The images so obtained are either of the total UV-VIS emission, or can be species selected by viewing through various narrow band pass optical filters. Mean velocities and velocity dispersions of the ablated species are calculated from these images and compared for the three different laser pulse duration times.

The results are discussed within the framework of recent theories concerning laser ablation with these pulse durations. The discussion will emphasise differences between the ablation processes occurring over these very different time scales.

6.1.1. Picosecond and Femtosecond laser ablation

The theoretical aspects of pico- and femtosecond ablation are discussed in Chapter 3. In the case of both of the studied materials, graphite and silicon, the solid melts in a much shorter time-scale than predicted via the two-temperature model after irradiation with short laser pulses. This can be explained by a very fast disordering of the lattice in these materials which can occur at an ionic temperature considerably lower than the melting temperature of the lattice. The laser source term couples directly into the electronic distribution, promoting the electrons into highly excited states. At high fluences, a large fraction of the electrons are promoted into antibonding orbitals. The system responds to the local differences in bonding interaction by ‘melting’ without any appreciable energy transfer between the excited ions and the lattice. This process is called ‘plasma annealing’ and can explain the fast transfer from the solid state into an electron-hole plasma.
6. Imaging of ablation plumes from KrF ablation

6.2. Experimental

The general aspects of the experimental set-up are discussed in Chapter 2. Since this set of experiments was performed in FORTH with different experimental apparatus to that available in Bristol, we will emphasise the specific differences between the two sets of apparatus.

The output of either a nanosecond (30 ns) or femtosecond (500 fs/5 ps) KrF (λ=248 nm) laser is focused onto a target in a stainless steel vacuum chamber (p = 1 \times 10^{-7} Torr). The interaction area comprises a rectangular spot with a size of 1.8 mm² (0.9 \times 2 mm) for the nanosecond pulse and 0.22 mm² (0.33 \times 0.66 mm) for the femto- or picosecond pulse, each of which is incident at an angle of 45°. The actual fluences used in the study are either 6.3 J/cm² or 10.3 J/cm² for the nanosecond, 3.6 J/cm² for the picosecond and 2.1 J/cm² for the femtosecond ablation of graphite. For the femtosecond laser ablation of silicon, a fluence of 2.5 J/cm² was used. Though the fluences used are very similar for the three laser pulse durations, the laser intensity is of course hugely different, since its magnitude depends on the pulse duration. A fluence of 5 J/cm² corresponds to an average intensity of 1.67 \times 10^8 W/cm² for the 30 ns, 1.00 \times 10^{12} W/cm² for the 5 ps and 1.11 \times 10^{13} W/cm² for the 450 fs laser pulses, respectively.

Spectroscopic measurements of the plume emission were obtained by focusing the optical emission through a quartz fibre bundle. The fibre abuts an adjustable entrance slit (set at 30 μm) to a spectrometer equipped with either a 600 lines/mm, a 1800 lines/mm or a 2400 lines/mm user selectable holographic grating, and a time-gated i-CCD camera (iStar 720D, Andor Technology).

The i-CCD camera images were obtained by decoupling the time-gated i-CCD array from the spectrometer and focusing the optical emission onto the 1024 \times 256 pixels diode array with a ~2:1 magnification. This yields a viewing window of ~ 8 \times 2 cm with a spatial resolution of ~ 84 μm per pixel.

The quartz fibre bundle and the i-CCD camera are also mounted differently (as described in Chapter 2) as compared with the Bristol experiment, specifically, they are mounted to view through a side flange in the chamber instead of the top flange. Thus, the viewing column for the spectrometer and the line of sight for the i-CCD array are in
the plane defined by the incoming laser light and the surface normal, as opposed to perpendicular to it.

6.3. Nanosecond laser ablation of graphite

6.3.1. Optical Emission Spectroscopy

The plume characteristics were first studied by wavelength resolved optical emission spectroscopy. A wavelength resolved spectrum of the ablation plume induced by nanosecond laser excitation (10.3 J/cm²) viewed at a distance of 5 mm from the target, along the surface normal, is given in Figure 6.1. From Figure 6.1a it is evident that the emission spectrum is dominated by the strong C⁺ ion emission feature at the wavelength of 426.8 nm. Other intense emission lines in the spectrum are the neutral C atom line at 658.7 nm, the C⁺ ion lines at 387.5, 392.2, 407.7, 589.4, 658.2, 723.6 nm and the second order peaks observed at 784.4 nm (2 × 392.2) and 853.6 nm (2 × 426.8). Confirmation that these are indeed second order lines involved monitoring through a long wavelength band pass filter that rejects light at wavelengths lower than 780 nm: these second order ‘long wavelength’ features also disappeared accordingly.
A more detailed picture of the emission spectrum is given in Figure 6.1b. This figure confirms that all recorded optical emission lines arising from 248 nm ablation of graphite in vacuum at 10.3 J/cm² can be attributed to either C atom or C⁺ ion excited species in the plume. At this distance only a very small feature attributable to C₂ molecular emission can be observed (at the band head of the Δν = 0 sequence of the d³Π₉-a³Π₈ Swan band system at ~ 516.5 nm).

As in 193 nm ablation (Chapter 4) all of the more intense emission lines of C atom and singly ionised C⁺ ions expected in this wavelength range are observed, illustrating that the excited species giving rise to the optical emission are produced by non-specific mechanisms during the laser ablation process. A direct excitation-de-excitation mechanism cannot explain the observed emission, given the distance of the viewing column from the ablation spot (5 mm), and the average lifetimes of the emitting states of excited C atoms and cations. As with the 193 nm ablation of graphite, the observed emissions are best explained by a cascade-down mechanism from longer-living Rydberg states.
The obtained results can be discussed in the framework of more extensive studies on the optical emission arising from 248 nm ablation and agree with the spectra obtained by Germain et al. and Yamagata et al. Germain et al. show that the threshold laser fluence for observation of \( \text{C}^+ \) ion emission at a distance of 10 mm from the target is 8 J/cm\(^2\) and the threshold laser fluence for observation of carbon dication emission is 17 J/cm\(^2\). They also observe a small amount of \( \text{C}_2 \) molecule emission close to the target at incident fluences <7 J/cm\(^2\). Yamagata et al. observed emission of neutral carbon atoms and small amounts of emission from \( \text{C}^+ \) ions at a fluence of 3 J/cm\(^2\) and at a distance of 10 mm from the target when ablating both poly- and single crystalline graphite. It must be noted that the relative intensity of the observed lines is highly dependent on the experimental set-up (base vacuum, distance of viewing column from target), the definition of the fluence and the spectral efficiency of the spectrometer for example, which could explain differences between the two studies.

Both studies observe that the \( \text{C}_2 \) molecular emission becomes predominant if the experiment is performed in a small pressure of nitrogen background gas. This illustrates that the excited dicarbon molecules are formed via collisional processes.

These earlier sets of studies investigate the ablation plume with optical emission spectroscopy, which only provides information on the radiative decaying excited species. In comparison Pappas et al. studied the ablation plume following 248 nm irradiation at fluences in the range of 1-10 J/cm\(^2\) with mass spectrometry. They observed that the ablation plume contains some fraction of dicarbon molecules maximising at a fluence of 5 J/cm\(^2\) and, presumably because of increasing laser-plume interactions, declining rapidly at higher fluences.

### 6.3.2. i-CCD camera images

In the present study, nanosecond laser ablation of graphite has been studied with i-CCD camera imaging at two different fluences, namely 6.3 J/cm\(^2\) and 10.3 J/cm\(^2\), to obtain information on the fluence dependency of the plume characteristics.

Analysis of the optical emission spectrum shows that the emission line at \( \sim 426.8 \) nm is the most intense \( \text{C}^+ \) ion emission and that all emission above 780 nm can be attributed to neutral C atom emission. A third region \( \sim 520 \) nm is the region of the brightest emission feature of the \( \text{C}_2 \) molecule, the \( \Delta \nu = 0 \) transitions of the Swan band.
6. Imaging of ablation plumes from KrF ablation

These wavelength regions can be monitored selectively by mounting appropriate optical filters in front of the i-CCD pixel array. The filters chosen for this study are a narrow band interference filter with a central wavelength of 427 nm to transmit just the emission of the intense C\(^+\) ion line, a long wavelength band pass filter that cuts off light of wavelengths below 780 nm to select emission features associated with the neutral carbon atom and a filter that selects light of a wavelength of 520 ± 20 nm to allow selective observation of electronically excited C\(_2\) molecules. The transmission of the filters is given in Figure 6.2 superimposed on the emission spectrum shown in Figure 6.1.

![Transmission curves for the three filters used in the i-CCD camera studies superimposed on the emission spectrum arising from 248 nm nanosecond ablation of graphite in vacuum.](image)

Figure 6.2: Transmission curves for the three filters used in the i-CCD camera studies superimposed on the emission spectrum arising from 248 nm nanosecond ablation of graphite in vacuum.

Figure 6.3 compares i-CCD camera images of (a) the total emission of the plume with the emission obtained by positioning the 520 nm, the >780 nm and the 427 nm transmission filters in front of the i-CCD camera (b)-(d) respectively. Application of these filters shows that the total emission can be divided into three components: one, fast, component related with the C\(^+\) ion emission, one slower component due to neutral
carbon atom emission and one component just in front of the target associated with \( \text{C}_2 \)
molecule emission. The dicarbon molecule emission is only observable close to the

target (< 5mm), thus explaining why the optical emission spectrum recorded at a
distance of 5 mm from the target surface does not show an intense \( \text{C}_2 \) molecule
emission feature.

Figure 6.3: Selected i-CCD camera shots observed with a time gate of 20 ns and a delay of 380 ns. (a) shows the total emission, (b), (c) and (d) show the emission arising from
\( \text{C}_2, \text{C}, \text{and C}^+ \), respectively. The arrow indicates the direction incident of the laser beam
(the laser beam is incident at 45\(^{\circ}\) but its projection on the recorded images is 0\(^{\circ}\)).

The i-CCD camera images are symmetric around the surface normal. This enables us to analyse the images by taking slices through the images parallel (defined as the y-axis) and perpendicular (defined as the x-axis) to the surface normal to obtain plots of signal versus distance from the target at a given time after the laser irradiation. Figure 6.4 shows the total emission of the ablation plume at a time delay of 380 nanoseconds after the ablating laser pulse together with a deconvolution of the total signal viewed along the surface normal (x-direction) into its respective components. The deconvolution shows that the total emission can be attributed into emissions from C atoms, cations or dicarbon molecules. The relative intensity of the \( \text{C}^+ \) ion emission at an incident fluence of 10.3 J/cm\(^2\) is far more dominant than that observed at 6.3 J/cm\(^2\), implying that the ionisation fraction of the plume scales with increasing fluence.
6. Imaging of ablation plumes from KrF ablation

Figure 6.4: Cuts through the central part of the i-CCD image of the plume along the surface normal with a time delay of 380 ns for the two fluences studied: (a) 6.3 and (b) 10.3 J/cm². The signal associated with the different components is fitted to the total signal.

The obtained signal versus distance plots show a single peaked behaviour for the C atom and cation distributions. This enables us to define a mean velocity and velocity dispersion for each of these components. A mean distance from the target at any given delay time can be inferred from the relevant i-CCD image by integrating a set of signal slices along the surface normal and finding the distance \( \bar{d} \) where the integrated distribution reaches half of the total integrated signal. This procedure reduces the sensitivity to noise, which is inevitably present in the experimental results.

A further elaboration involves defining the points where 25% and 75% of the signal is reached as the Half Width at Half Maxima for the rising (towards vacuum) and the trailing (towards target) edge. The sum of the thus obtained Half Width at Half Maxima provides an experimental definition of the Full Width at Half Maximum and the difference between both gives an idea of the asymmetry of the distributions. Perpendicular slices (x-direction) through the images are also obtained at distances close to \( \bar{d} \) in order to define the dispersion along an axis orthogonal to the surface normal (x-direction) of each emitting component within the plume. These latter distributions are highly centro-symmetric and can easily be fitted by a normal Gaussian distribution, which again serves to remove the noise from the experimental data.
6. Imaging of ablation plumes from KrF ablation

The i-CCD images obtained by monitoring the emission through the filter centred ~ 520 nm have to be processed more carefully. The C₂ molecule emission distribution obtained in these images is contaminated by signal from C atom and cation lines lying in the active region of the optical filter. These images are deconvoluted by subtraction of the C⁺ ion and atom emission from the obtained signal to obtain the distribution of the C₂ emission. To obtain a functional form for the emitting C atom and cation distributions their experimental distributions have been fitted to a split Gaussian with an independent Half Width at Half Maximum for the trailing and rising edges. This type of function was chosen for its large flexibility; as Figure 6.5 shows the function mimics the observed distributions closely. The fitted functions are used to subtract the signal associated with the C atom and cation emission from the 520 nm images. Although there is no unique scheme for subtracting the signals, the data shown in Figure 6.5 indicate that an excited dicarbon molecule distribution remains just in front of the target even at late time-scales. Since the subtraction scheme is somewhat arbitrary we do not report any velocities for the dicarbon molecule.

Figure 6.5: Cuts along the surface normal through (a) the C atom and (b) C⁺ ion images, together with the fitting functions used for these respective species and (c) deconvolution of the 520 nm signal to yield an emitting C₂ molecule distribution.
With this deconvoluted signal attributable to the emitting C\textsubscript{2} molecules and the fitted distributions for the C atoms and cations, we can build a model of the structure of the emitting species in the plasma along the surface normal. The model distribution is given in Figure 6.6. From this model we can infer that both the cation and atom distribution have developed a non-zero Centre of Mass velocity distribution. Such density distributions are observed for an adiabatically expanding gas after formation of a Knudsen layer\textsuperscript{22}. The C\textsubscript{2} molecule distribution peaks at the target surface and declines monotonically into the vacuum. This model also shows that the trailing edge (towards the target) of the C atom distribution has a finite ($\sim$ 60\% of the peak signal) density at the target surface. Since this model distribution is derived from slices along the surface normal this estimate is an overestimation, the signal has to scaled by the distance from the target surface to get a more exact estimate of the radial variation of the density.

![Figure 6.6: Model distribution of the ablation plume from graphite at an incident fluence of 10.3 J/cm\textsuperscript{2} and a delay time of 380 ns.](image)

Plots of mean distance versus delay time are shown in Figure 6.7 for both fluences studied. These show the mean distance scaling linearly with time. The line fitted to the experimental points intercepts the origin of the plot within the experimental error, confirming that the onset of ablation occurs at time equals zero. The gradient of
this linear relationship corresponds to the mean velocity of the particles. The dispersion of the velocities is indicated by the FWHM of the curves. The calculated velocity dispersion perpendicular to the surface normal is also given in Figure 6.7.

Figure 6.7: Experimental results for a fluence of (a,b) 6.3 J/cm² and (c,d) 10.3 J/cm² (a) and (c) show the centre of mass velocities for the C atoms and cations with their respective FWHM’s indicated by the dashed lines. (b) and (d) show the FWHM’s perpendicular to the surface normal for both fluences.

The deduced velocities are given in Table 6.1. Comparing the two fluences one can conclude that the velocities of the C atom and cation signals increase slightly with the fluence. The velocity of the emitting C atoms is less than half that of the emitting C⁺ ions. The velocity dispersion of the C⁺ ion signal increases with increasing fluence whereas that for the C atom distribution decreases. Overall, the velocity distributions are overall relatively insensitive to the difference in applied laser fluence.
6. Imaging of ablation plumes from KrF ablation

Table 6.1: Calculated velocities and velocity dispersions for emitting C atoms and cations.

<table>
<thead>
<tr>
<th></th>
<th>Mean (km/s)</th>
<th>FWHM (km/s)</th>
<th>6.3 J/cm²</th>
<th>10.3 J/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C⁺⁺</td>
<td>16.0 ± 0.4</td>
<td>16.8 ± 0.9</td>
<td>41.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>C⁺⁺</td>
<td>15.5 ± 0.4</td>
<td>8.8 ± 0.8</td>
<td>9.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Rising edge</td>
<td>31.5 ± 2.4</td>
<td>31.3 ± 2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trailing edge</td>
<td>5.8 ± 0.5</td>
<td>7.2 ± 0.8</td>
<td>7.2 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Perpendicular</td>
<td>40.3 ± 3.0</td>
<td>46.4 ± 6.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C⁺⁺</td>
<td>31.5 ± 2.4</td>
<td>31.3 ± 2.0</td>
<td></td>
</tr>
</tbody>
</table>

The results of this nanosecond ablation study should be compared with those reported in references 11 and 1. In these earlier studies the ablation plume arising from KrF ablation of graphite at fluences of 6.7 and 17.7 J/cm² were similarly studied by wavelength selected i-CCD camera imaging and photon counting spectroscopy. As in the present study the plume emission could be subdivided into three main components, each with a distinct mean velocity. When ablating with a fluence of 6.7 J/cm², the total signal could be deconvoluted into a fast component consisting of C⁺ ion emission ($v = 35$ km/s), a component consisting of neutral C atom emission ($v = 11$ km/s) and a slow component attributable to C₂ molecule emission ($v = 3$ km/s). A fourth component was evident at higher ablation fluences (17.7 J/cm²) and was described in terms of jets of excited C₂ molecule emission arising from hydrodynamical instabilities. The present results agree not just qualitatively but also quantitatively with the earlier findings, illustrating the high degree of reproducibility possible with these experiments.

6.3.3. Results and Discussion

Optical emission accompanying nanosecond laser ablation is very long lived relative to the average radiative lifetimes of the excited levels that give rise to the observed emission lines as indicated previously in this chapter and in Chapter 3. This observation holds for ablation of all materials studied in this thesis, indicating that there must be some general mechanism for explaining this behaviour. The rationale given for
this behaviour is that observed emission arises at the end of a slow ‘cascade down’ mechanism as shown in Figure 6.8. The cations generated via the ablation event can recombine via third-body recombination with an electron, given a high enough plume density. The product of such recombinations are likely to be in Rydberg states with high principal quantum number, \( n \), since such recombinations involve the least energy transfer to the third body. Many of these Rydberg states will not only possess a high principal quantum number but also a high angular momentum quantum number, \( \Delta l \). Many of these highly excited states are very long lived, since their radiative decay is restricted by the selection rule \( l = \pm 1 \). Such mechanisms will lead to a slow cascade down mechanism, which can account for the apparent delayed emission by the observed species in the plume.

![Simplified Grotrian diagram for atomic carbon.](image)

Figure 6.8: Simplified Grotrian diagram for atomic carbon. TBR represents the three body recombination, which leaves the products in highly excited Rydberg (R) states. These Rydberg states are presumed to decay by a slow radiative (SC) cascade down, including the observed transitions, en route to the ground state.

Another general process in nanosecond ablation, as pointed out previously, is interaction between the incident laser light and the produced plasma. The interaction between the plasma and the plume is governed by inverse Bremsstrahlung and multiphoton ionisation. Inverse Bremsstrahlung is less important for shorter wavelengths as discussed previously in the 193 nm work. Multiphoton ionisation on the
other hand is relatively unlikely for carbon atoms in the ground state, since its high ionisation potential (11.26 eV), means that three KrF photons are required for this process. Pappas et al. 9 pointed out in their study on KrF laser ablation that there is a resonance between the C atom 2p'3s' (1P1, 0) ← 2p2 (1S0) transition (247.93 nm) and the KrF laser wavelength. If the 1S0 level is populated a resonantly enhanced two photon ionisation should occur since the energy of the transition lies within the spectral lineshape of the laser transition. The KrF laser intensity at 247.93 nm is estimated to be only ~15 % of the peak intensity, while the C(1P1, 0→1D2) transition overlaps much closer with the peak of the ArF lasing transition (at ~90% of the peak intensity), causing a higher ionisation fraction in the case of ArF laser produced plumes (as depicted in Figure 6.8).

The particle ejection behaviour of graphite under nanosecond 248 nm laser irradiation was also investigated in the mass spectrometric study of Krajnovich 7 at laser irradiation fluences just above the ablation threshold (0.3-0.7 J/cm2). Cn clusters with n ≤ 5 are observed in this study but the dominant products are carbon atoms, dicarbon and tricarbon molecules. The relative yields of the C:C2:C3 fractions were estimated as 29:18:51. Since the fluences are just above the ablation threshold this study provides perhaps the clearest picture of the fundamental ejection mechanisms of graphite under 248 nm irradiation. At higher laser photon flux many of the molecular products will break down to form C atoms. This is supported by the aforementioned observations of Pappas et al. 9, which show an increasing C2 molecule yield up to 5 J/cm2. Above this fluence the relative yield of the C2 molecule species declines sharply, consistent with dissociation of the dicarbon molecules induced by the laser photons.

The ejection and laser excitation behaviour can also explain the structure of the plume at the studied fluences, namely a fast C+ ion emission signal, followed by a slower C atom distribution. This is compatible with the laser-induced dissociation of the ablated products followed by laser-induced ionisation of the product C atoms in the plume. The front edge of the ablation plume is preferentially excited by the laser light. The temperature rises in the interaction region and causes a pressure rise, which accelerates the heated zone to a higher terminal velocity.

C2 emission is observed at a fluence of 10.3 J/cm2 although, as suggested above, most of the directly ejected C2 molecules are dissociated by the laser photon flux. This implies a different creation mechanism for the observed excited C2 molecules compared
with the ground state C₂ molecules. Geohegan et al.¹ showed via photon counting spectroscopy that the C₂ emission region also contains emission from higher carbon clusters and even black body radiation from small graphite particles. This indicates that the excited, radiatively decaying, C₂ molecules are formed in a collisional regime just in front of the target. As shown in Figure 6.6, a significant fraction of the C atom distribution is remaining at the target surface. This fraction encounters, and collides, with the forward flow of particles evaporating from the target during the laser irradiation. The collisions in this high-pressure region can produce the higher mass carbon fragments observed or more likely even larger Cₙ fragments undergo collisional dissociation to produce the C₂ fragments.

6.4. Picosecond and Femtosecond laser ablation of graphite

6.4.1. Optical Emission Spectroscopy

Figure 6.9 shows the wavelength resolved optical emission spectrum from a graphite target after picosecond radiation (5ps - 3.6 J/cm²) at three different distances, at 0.5 mm, 1 mm and 5 mm from the target. As in the case of nanosecond ablation the spectra are governed by the strong emission feature of the C⁺ ion at 426.8 nm. Other strong emission features are: the C⁺ ion lines at 392.1, 589.2, and 658.3 nm and the carbon dication lines at 406.8, 418.7, 465.1 and 466.6 nm. The corresponding emission spectra observed following femtosecond irradiation (450 fs - 2.1 J/cm²) of graphite are given in Figure 6.10. Comparing this with Figure 6.9, we observe that the emission behaviours arising in the two different regimes are very similar, but noticeably different from the emission observed in the case of nanosecond ablation of graphite.
Figure 6.9: Optical emission following picosecond laser ablation of graphite in vacuum monitored at (a) 0.5 mm, (b) 1 mm and (c) 5 mm from the target. The inset shows the spectrum around 520 nm in expanded detail.
Figure 6.10: Optical emission following femtosecond ablation of graphite in vacuum monitored at (a) 0.5 mm, (b) 1 mm and (c) 5 mm from the target. The inset shows the spectrum around 520 nm in expanded detail.

Neither of the spectra exhibit any emission features associated with excited C atoms, and the total emission intensity is much less than in the nanosecond case. This is also evident by the bare eye; the emission plume is almost indiscernible except for the spot of the laser footprint on the target. This can be compared with the removal rate for the different laser pulse lengths; for the nanosecond laser ablation the removal rate is 500 nm/shot, at a laser fluence of 6.3 J/cm², while for femtosecond laser ablation it is only ~ 140 nm/shot, at a laser fluence of 2.1 J/cm², as measured by stylus profilometry. It has to be noted that the spot size of the nanosecond laser on the target (1.8 mm²) is much larger than the femtosecond laser (0.22 mm²) giving a much higher removal rate for the nanosecond ablation compared with femtosecond ablation.
The spectrum taken just in front of the target (0.5 mm) contains a small amount of molecular C\textsubscript{2} emission, as shown in the insets to Figure 6.9 and Figure 6.10, evident from the rise in signal at ~516 nm, associated with the $\Delta v = 0$ progression in the Swan band system. A second observable feature in spectra taken very close to the target is a broad band emission in the range of 360 - 450 nm (observable in Figure 6.11a). This might be attributable to hot electrons in the plume emitting photons at wavelengths predicted by the Bremsstrahlung equation, or broad band emission of tricarbon radicals. In addition the line spectrum is superimposed on a continuum emission arising from black body radiation of large particles. Spectra recorded at 3 and 5 mm do not exhibit any of these broad emission features, demonstrating that they are confined to the high-pressure region just in front of the target. The spectra taken at longer distances show a radiative decay analogous to that observed in the nanosecond laser ablation experiments.

The optical emission close to the target has also been studied in time gated mode, with a long time delay (0.1 $\mu$s) between the laser ablation event and the start of the time gate on the i-CCD. Given such a time delay, it was expected that the fast plasma plume should have propagated far beyond the viewing column; the i-CCD camera images confirm this expectation. The displayed spectrum is corrected for the wavelength dependent reflectivity of the grating and the quantum efficiency of the i-CCD array by multiplying the signal by a wavelength dependent function, which was derived from the relevant efficiency curves provided by the manufacturers. This corrected spectrum is given in Figure 6.11b, and shows weak molecular emission due to C\textsubscript{2} molecules ($\Delta v = -1, 0$ and 1 Swan band transitions) superimposed on the black body radiation from larger particles. The 360-450 nm emission feature has disappeared, suggesting that this feature is associated with fast electrons in the plume rather than slow moving C\textsubscript{2} radicals. The wavelength dependence of the black body radiation curve is reproduced well assuming a temperature of 3050 ±150 K. Very similar temperatures can be derived by fitting the black body radiation background signal underlying the structured spectra recorded at early times for both picosecond and femtosecond laser irradiation regimes.
6. Imaging of ablation plumes from KrF ablation

Figure 6.11: Emission spectra corrected for the wavelength dependent quantum efficiency of the grating and the i-CCD array, recorded at (a) early and (b) late time-scales following 248 nm ablation of graphite in vacuum using 450 fs laser pulses.

These optical emission results can be compared with those reported by Rode et al. in their 1064 nm high repetition rate (76 MHz) 60 ps laser ablation studies of graphite in vacuum using fluences of 0.17 J/cm² (corresponding intensity = 2.8 ×10⁹ W/cm²). This is, to the best of our knowledge, the only comparable study reporting optical emission following short pulse duration laser ablation of graphite. Their emission spectrum shows carbon cation and dication emission, weak radiation from one neutral C atom line at 248 nm and no emission from C₂. This might be due to the position of their viewing column relative to the target, which is not indicated in the study. They infer a rough estimate of the plasma temperature, between 1.5 and 6 eV. In addition, the temperature of the target and of particulates in the plume is calculated from fitting the spectrum of the accompanying black body radiation, yielding values between 2500-3500 K. These observations and values are remarkably similar to those obtained in this study, with the differences likely attributable to differences in experimental set-up. This suggests that the optical emission following laser ablation of graphite in vacuum with laser pulse duration < 100 ps is broadly similar, and independent of the precise time duration or the laser wavelength.
6. Imaging of ablation plumes from KrF ablation

6.4.2. i-CCD camera images

As in the nanosecond studies, the total emission observed by time-gated i-CCD imaging can be deconvoluted by the application of filters, as demonstrated in Figure 6.12 for the cases of both picosecond and femtosecond laser excitation. The plume mainly consists of emission originating from the carbon cation and the dicarbon molecule. As demonstrated in the wavelength dispersed optical emission spectra there is no noticeable emission from neutral carbon atoms. Note that this does not necessarily imply that there is no atomic carbon in the ablation plume, since the C atoms might be ejected in non-emitting states (e.g. the ground state).

The emissions from the ablation plumes in the picosecond and femtosecond ablation experiments appear very similar. In both cases the characteristics of the emitting species are comparable with the behaviour observed under nanosecond laser ablation excitation, except for the absence of the neutral atomic carbon component. The C+ emission appears as a fast distribution, while the C2 molecule emission is confined to a small volume just in front of the target surface. This suggests similar excitation mechanisms in the case of all three pulse durations.
Figure 6.12: i-CCD camera images of the emission plume recorded with 20 ns time gate starting 120 nanoseconds after laser irradiation of the graphite target. 1) picosecond radiation and 2) femtosecond radiation, a) Total signal, b) emitting C\(^{+}\) signal and c) emitting C\(_2\) molecule signal.

The total emission can again be deconvoluted into its respective parts, as shown for both pulse durations in Figure 6.13. The total signal is fitted reasonably well in terms of just these two distributions, though the fit for the picosecond ablation fails to include the whole signal, and the fast edge (towards the vacuum) of the total signal is more pronounced than the rising edge of just the fast C\(^{+}\) species. One possible source of extra signal could be emitting C\(^{2+}\) ions travelling faster than the C\(^{+}\) ions, but this remains a hypothesis since we did not experimentally measure the velocity distribution of the C\(^{2+}\) ions. We also note that this fast component is not observed on the total signal image recorded with femtosecond excitation, indicating that it might be an experimental artefact.
6. Imaging of ablation plumes from KrF ablation

Figure 6.13: Deconvolution of the total signal image along the surface normal at 120 nanoseconds after laser irradiation and with a time gate of 20 ns for (a) picosecond and (b) femtosecond laser ablation.

The data reveal a slow component to the total emission close to the surface due to C₂ emission and a fast signal that can be assigned to emission of C⁺ ions. The velocity of the C⁺ ions is calculated in the same way as for the nanosecond images. The mean velocity and its dispersion are illustrated in Figure 6.14, and compared with those obtained in the nanosecond ablation experiments in Table 6.2.

As in the nanosecond laser studies, the distributions recorded with the ~ 520 nm filter contain signal from electronically excited C⁺ ions and C₂ molecules. The spectrum is deconvoluted by subtracting an approximately weighted C⁺ component from the total image. As with the nanosecond ablation of graphite, we do not attempt to infer any velocity for the resulting C₂⁺ distribution.
Figure 6.14: Mean distance versus time plots for picosecond (a,b) and femtosecond (c,d) laser ablation. (a) and (c) are the centre of mass velocities for the C\(^+\) ions with their FWHM’s indicated as dashed lines. (b) and (d) are the distance FWHM’s perpendicular to the surface normal for both pulse durations, measured at the mean of the distribution along the surface normal.

<table>
<thead>
<tr>
<th></th>
<th>Velocity (km/s)</th>
<th>FWHM (km/s) (y-direction)</th>
<th>FWHM (km/s) (x-direction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanosecond</td>
<td>41.2 ± 0.5</td>
<td>12.9 ± 0.8</td>
<td>40.3 ± 3.0</td>
</tr>
<tr>
<td>Picosecond</td>
<td>51.2 ± 1.0</td>
<td>16.0 ± 2.1</td>
<td>57.1 ± 6.2</td>
</tr>
<tr>
<td>Femtosecond</td>
<td>63.2 ± 1.1</td>
<td>14.2 ± 4.1</td>
<td>63.6 ± 8.0</td>
</tr>
</tbody>
</table>

Table 6.2: Mean velocities and velocity dispersions of electronically excited C\(^+\) ions in pico- and femtosecond ablation of graphite compared with the nanosecond ablation results. The x- and y-directions are perpendicular to, and along, the surface normal, respectively.

The calculated centre of mass velocity for the emitting C\(^+\) ions increases with decreasing laser pulse duration, while the FWHM along the surface normal (y-direction) shows little dependency on the laser pulse duration. The FWHM perpendicular to the surface normal scales with the Centre of Mass velocity along the surface normal. This
implies that the excited C\(^+\) ions are ejected in a constant solid angle independent on the pulse duration. The distributions are relatively narrow and forward peaked in all cases.

These figures can be compared with those presented by Qian et al.\(^{12}\), although the fluences (10-600 J/cm\(^2\)) and laser intensities (\(1 \times 10^{14} - 6 \times 10^{15}\) W/cm\(^2\)) used in their study are much higher than the fluences used in the present work. Their Time of Flight ion transients show a broad distribution (see Chapter 3) with a pronounced double peak behaviour at these high fluences, these have been interpreted in terms of a thermal peak, with velocity \(\sim 60\) km/s, and a suprathermal peak, with velocity \(\sim 240\) km/s. A more detailed discussion of the origin of this plume splitting was given in Chapter 3.

Only the thermal component of the plume is observed in the present i-CCD camera imaging study. This correlates with the much lower fluence and laser intensity used here. As argued in reference 12, the relative intensity of the suprathermal peak is highly dependent on the fluence used. Note, however, that a suprathermal component cannot be explicitly excluded in the present ablation study, since, with i-CCD camera imaging, only emitting species are observed. It could be that higher velocities imply less opportunity for three body recombination reactions (because of the radial thinning of the plasma) and thus a lower probability of forming, and thus detecting, emitting species via this mechanism.

The distributions can again be fitted and modelled: the model distribution is shown in Figure 6.15. Comparing these figures with those derived from imaging the nanosecond ablation emissions (Figure 6.6) we observe a higher plume density for the nanosecond ablation at the target surface at a given time delay since the existence of C\(^+\) in the ablation plume following nanosecond excitation. In apparent contradiction with this observation, however we still observe a bright spot of C\(_2\) emission just in front of the surface which, by analogy with the nanosecond irradiation results, we attribute to a collisional channel. Possible reaction routes by which emitting dicarbon molecules could form from recombination of a C\(^+\) ion and a carbon atom are given in equations (6.1), (6.2) and (6.3) where, as usual, asterisks indicate an excited state species and \(\text{TB}\) stands for Third Body. The reaction given in equation (6.1) is highly improbable since it is a four body reaction, while the reaction given in equations (6.2) is also unlikely since the reaction involves a transient ionic species, C\(_\ast\). The reaction given in equation (6.3) is more plausible, but involves excited C atoms for which there is no evidence in the emission spectrum.
6. Imaging of ablation plumes from KrF ablation

Figure 6.15: Model distribution of femto- and picosecond laser ablated plume at a time delay of 120 ns derived from taking slices through the images along the surface normal. (a) the fitting function for the $C^+$ ion emission arising in the picosecond laser ablation of graphite compared with the experimental signal (b) the model distributions for the $C^+$ ion and the dicarbon molecule emissions arising in the picosecond pulse laser ablation, (c) and (d) equivalent graphs for femtosecond laser ablation.

\[
C^{++} + C + e + TB \rightarrow C_2^{*} + TB^* \tag{6.1}
\]

\[
C^{++} + C + TB \rightarrow C_2^{++} + TB^* \tag{6.2}
\]

\[
C_2^* + e + TB \rightarrow C_2^* + TB^* \tag{6.3}
\]

\[
C^{*} + e + TB \rightarrow C^* + TB^* \tag{6.4}
\]

\[
C^* + C + TB \rightarrow C_2^* + TB^* \tag{6.5}
\]
Given the conceptual difficulties associated with each of these proposed mechanisms we suggest that the region of \( \text{C}_2 \) emission is formed by one or more alternative reaction pathways involving non-emitting species. The short laser pulse duration means that it is very unlikely that the laser light will be absorbed by the ejected species. Since a large part of the total ablated material is ejected via a thermal mechanism (according to the two-temperature model) the ablation plume will consist of an abundance of ground-state species. Possible mechanisms to form electronically excited \( \text{C}_2 \) are given in (6.4) and (6.5).

\[
\begin{align*}
\text{C} + \text{C} + \text{TB} &\rightarrow \text{C}_2^* + \text{TB}^* & (6.4) \\
\text{C}_n^* + \text{e} &\rightarrow \text{C}_2^* + \text{C}_{n-2} \\
\text{C}_n^* + \text{C} &\rightarrow \text{C}_2^* + \text{C}_{n-1} & (6.5) \\
\text{C} + \text{surface} &\rightarrow \text{C}_2^* + \text{surface} & (6.6)
\end{align*}
\]

The first mechanism (6.4) is a three body recombination of two ground state carbon atoms ejected by the target via a thermal mechanism, the second mechanism (6.5) represents dissociative (electron or atom) recombination of larger particulates and the third proposed mechanism (6.6) is reaction of a carbon species with the target surface. The existence of these large particulates has already been demonstrated via optical emission spectroscopy of the black body radiation evident at long time-scales. Their deduced temperature (~3000 K) is below the melting point of graphite (4300 K \(^{24}\)). These large particulates are visible to the bare eye as bright incandescent tracks originating from the focal volume. Figure 6.16 shows tracks generated by these particulates at different delay times. The tracks indicate that the particulates have a well-directed forward velocity and that they originate from the laser interaction spot, thereby proving that the particulates are associated with the laser ablation process.
6. Imaging of ablation plumes from KrF ablation

Figure 6.16: i-CCD images of large particulates observed using a time gate of 50 μs at different times, (a) 40 μs, (b) 60 μs and (c) 80 μs after the laser pulse.

A distribution for these particulates can be obtained by summing up a number of shots (typically 200 shots) viewed with a sufficiently small time gate to ensure that the particulates show up as well defined dots in the pictures instead of tracks. A selection of such images obtained at different delay times is shown in Figure 6.17. Since the summed i-CCD camera images show a continuous distribution we can treat these pictures in the same way as the optical emissions of the atomic and ionic species in the plume. The centre of mass distance versus the time can be plotted out and is given in Figure 6.18, noticeably, the obtained curves do not follow linear relationships, as opposed to the atomic/ionic emission. The angular distribution of the total signal at any given delay time was calculated by taking radial slices through the images and summing the total signal above the background level. Since all of these distributions had a very similar angular form, they were finally summed to give an average angular distribution. The average angular distributions so obtained, for both the pico- and femtosecond ablation studies, are shown in Figure 6.18 together with a plot describing the definition of the angle quoted in these distributions. Table 6.3 summarises the results.
Figure 6.17: Integrated image (200 shots) of the black body radiation associated with the large particulates recorded with a gate width of 1 µs at different time delays, (a) 40 µs, (b) 80 µs and (c) 130 µs for the femtosecond laser ablation of graphite in vacuum.

Figure 6.18: (a) Centre of mass velocity with the first order exponential decay fitting curves to the points (red lines), and (b) angular distribution for the picosecond ablation. (c), (d) corresponding graphs for femtosecond laser ablation. (e) Cartoon of the deconvolution the angular distribution.
6. Imaging of ablation plumes from KrF ablation

<table>
<thead>
<tr>
<th>Initial Velocity (m/s)</th>
<th>Terminal Velocity (m/s)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picosecond</td>
<td>100</td>
<td>29.6 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>23.7 ± 0.8</td>
</tr>
</tbody>
</table>

Table 6.3: Initial COM velocity of the particulates (calculated by the slope of the line defined by the origin and the first point) and terminal velocity (calculated by fitting the points to a line) along the surface normal and the value for the fit of the angular distribution ($n$) to a $\cos^n \theta$ distribution.

The calculated terminal velocity for these particulates generated both with picosecond and femtosecond pulses is around 25 m/s and the initial velocity is calculated as 100-160 m/s. This, of course, implies that the particles decelerate during their time of flight. Important to note at this point is that the density of the particulates ejected every laser shot, as shown in Figure 6.16, is too low (~100 particulates/shot) to assume any interactions between them at later time delays. Also the plasma plume at these time delays has propagated far beyond the viewing zone, inferring that the particulates are propagating in a field free regime (without any forces applying on them). This assumption is supported by the observation that the recorded tracks in Figure 6.16 are linear without any deflections or kinks, which would imply force field gradients or collisions.

A closer look at the images in Figure 6.17 reveals that an intense region remains just in front of the surface which could be the reason for this apparent deceleration. A possible interpretation of this observation is that, since the particles are created with a certain temperature and with a given kinetic energy, the smallest particulates will exhibit the highest velocity while bigger particulates will propagate with smaller velocities. The smaller particulates will also cool down faster via black body radiation, and will become undetectable earlier in time (because of the red shift) given the wavelength dependent quantum efficiency of the CCD array. So the velocity distribution would apparently slow down at later time delays by this mechanism.

The initial velocity can be correlated with the particle size, assuming the initial velocity distribution of the particulates is Maxwellian, as proportional to $\sqrt{T/M}$ - where $T$ is the melting/sublimation temperature of graphite (~4300 K) and $M$ is the
particulate mass. The particle mass corresponds to $C_n$ clusters of mean particle size $n \approx 275$ assuming an initial velocity of 160 m/s.

The observation that the velocity distribution is highly forward peaked, as shown in Figure 6.18 and summarised in Table 6.3, implies that the particulates are ejected via a different mechanism than a thermal ejection mechanism, which would exhibit $\cos \theta$ behaviour. Care has to be taken of the fact that the images are a two dimensional projection of a three dimensional event in the interpretation of this observation. The squashing of a 3-D event in a 2-dimensional picture can induce a higher forward peaking of the plume because of overestimation of the density of the dense regions within the plume, in this case the region along the surface normal, although it is expected that this is not the sole reason for this forward peaking. Another contributing factor is that the particulates are ejected from a microscopically rough surface which enhances also the yield of forward directed material. Additionally, of course, we recognise that these macroparticles are ejected simultaneously with, and into a stream of, light, fast moving atomic species. As shown above, the velocity distributions of these latter species are forward peaked along the surface normal; any momentum transfer between atoms and macroparticles in the early stages of the expansion should thus also contribute a net forward velocity to the latter.

The temperature of the particulates calculated by fitting the emission spectrum attributed to black body radiation indicates that they are solid. This statement has been proven in a more direct way by putting a substrate in the vacuum chamber at a distance of $\approx 3$ cm. A large number of the ejected particulates scatter back from the surface of the substrate as shown in Figure 6.19. This behaviour can only be explained by assuming the particulates ejected as solid particles of graphite and propagate through the vacuum cooling down during their time of flight by radiation.
6. Imaging of ablation plumes from KrF ablation

Figure 6.19: i-CCD camera images of large particulates reflected from the surface, at femtosecond laser ablation, the time delay is 50 μs and the gate is 500 μs.

6.4.3. Analysis of laser-irradiated region

The laser-irradiated region has been analysed by Raman spectroscopy and SEM imaging. Selected SEM pictures are presented in Figure 6.20. The surface of the irradiated region appear to have undergone a phase transition correlated with melting behaviour and a resolidification to what appears to be a glassy carbon melt. The melt looks smooth suggesting that this melting behaviour is not associated with explosive melting or phase explosion. Phase explosion occurs when the material is heated near to its critical temperature. Analysis of the black body radiation of the ejected particulates indicates that this temperature is not reached during either the pico- and femtosecond ablation of graphite.

Figure 6.20: (a) Low and (b) higher resolution SEM images of the irradiated spot. (a) Shows the ablation track and (b) shows a detail of the graphite surface, post ablation.
The proposed phase transition during ablation is supported by Raman spectroscopy. Typical Raman spectra of non-irradiated graphite and the target surface post ablation are presented in Figure 6.21. These spectra indicate that the graphite in the irradiated spot has undergone a phase transition from graphite to amorphous carbon containing some fraction of tetrahedral co-ordinated carbon.

![Figure 6.21: Selected Raman spectra of the target (a) non-irradiated graphite target (b) target after irradiation.](image)

These results can be compared with those obtained by Shirk et al. They use Raman spectroscopy to compare the surface of the target before and after ablation for laser pulses with durations varying from 120 ns to 20 ps. This study inferred the operation of a surface phase transition towards DLC at all pulse durations studied, consistent with the present results.

### 6.4.4. Analysis of deposited films

Films have been deposited for a duration of 20,000 laser pulses in vacuum with the femtosecond laser. The deposited films have also been analysed by Raman spectroscopy and SEM imaging. The SEM images show a nanometer smooth film, with
a large amount of micrometer sized (0.5-1 μm) particulate inclusions, a typical picture is shown in Figure 6.22. This observation is consistent with the observed abundance of ejected particles.

Figure 6.22: SEM picture of the film deposited via femtosecond laser ablation (2.1 J/cm²) at a distance of 5 cm.

Raman spectra of this film are given in Figure 6.23. The Raman spectra are consistent with a thin film of amorphous carbon with graphite particulates included within the film. As discussed in reference 25, the observed double peak behaviour in the Raman spectrum indicates a poor quality amorphous carbon film. The film is clearly very thin, given the obvious strength of the Si feature at ~960 cm⁻¹ in comparison with the features from the film. The large graphitic particulates embedded in the film exhibit peak broadening as compared to the Raman spectrum of the graphite target (Figure 6.21) implying that the deposited particulates are subjected to internal stresses.
Figure 6.23: Raman spectra of the deposited films (b) Raman spectrum focused at a smooth part of the film (a) Raman spectrum focused on an micrometer size embedded particle. The feature at ~960 cm\(^{-1}\) is a feature of the Si substrate used.

The study of Qian et al.\(^{12}\) provides a comparison for our investigation. The results presented in their study show DLC films with a large number of micron sized particles embedded in the film. The sp\(^3\) fraction within the film (50-60 \%) is inferred by Raman spectroscopy and EELS. In their study, the poor quality of the produced films was deduced to correlate with the occurrence of the suprathermal peak. It is well known that the sp\(^3\) fraction of the DLC films deposited via laser ablation is correlated with the kinetic energy of the ions impacting on the substrate\(^{26}\). The consensus view is that carbon ion kinetic energies \(~100\) eV (40 km/s) are 'ideal'. Lower kinetic energies result in lower compaction of the film, while higher kinetic energies tend to disrupt the lattice of the film, both leading to inferior film quality. The films deposited in this study also showed poor quality, although the thinness of the films prevented quantification of this observation.
6. Imaging of ablation plumes from KrF ablation

6.5. 248 nm femtosecond laser ablation of Silicon(111)

6.5.1. Optical Emission Spectroscopy

As a comparison, the 248 nm femtosecond laser ablation of silicon in vacuum was also studied via optical emission spectroscopy and i-CCD camera imaging of the plume. Optical emission spectra of the ablation plume, recorded at distances of 0.5 and 5 mm from the target surface, are shown in Figure 6.24. The most intense emission lines can be attributed to electronic transitions of the silicon atom (390.6 nm), the silicon cation (385.6, 412.8, 505.6 nm) and the silicon dication (380.7, 456.8 nm). In addition, spectral lines attributable to emission from the silicon trication (408.9, 411.6 nm) are discernible. Although the degree of ionisation is higher than in the graphite case, this is in part a reflection of the lower ionisation potential. Given that we observed optical emission from Si$^{n+}$ ions with $n < 4$, we assume the presence of Si$^{4+}$ cations in the ablation plume. The total ionisation energy associated with formation of the silicon tetracation is 107.13 eV while the energy necessary to obtain the silicon pentacation is much higher (273.9 eV). By way of comparison, the energies necessary to obtain the carbon trication and tetracation are 83.53 eV and 148.02 eV, respectively. The observation of C$^{2+}$ emission (from e$^{-}$ + C$^{3+}$ recombination) but not C$^{3+}$ emission in the case of 248 nm femtosecond ablation of graphite implies that the degree of electronic excitation of the plume following ablation of silicon is of similar magnitude to that found in the case of graphite.
Figure 6.24: Optical emission spectra of the plume arising in the femtosecond 248 nm laser ablation of silicon recorded at distances of 0.5 and 5 mm from the target.

The optical emission of silicon at 0.5 mm consists of broad emission features with a superimposed line spectrum. The spectral lines are significantly broadened, compared to those in spectra taken at 5 mm, presumably because of pressure broadening due to the high charge density in this region. The emission spectra taken using the graphite target exhibit similar behaviour, although less pronounced. The broad emission feature centred around 400 nm is attributable to Bremsstrahlung arising from the electrons in the plume. In addition the spectrum exhibits a continuum emission attributable to black body radiation. At distances further from the target (5 mm) the spectrum displays well-resolved emission lines.

To obtain additional time resolved information about the optical emission, wavelength resolved spectra have been recorded in 50 μs time gates at a distance of 5 mm. A rough indication of the velocity for the different species contained within the plume can be inferred from such time resolved spectra by plotting the intensities of selected emission lines versus the delay time, and then calculating the velocity of the emitting species by dividing this distance by the time where the emission peaks. The
‘Time Of Flight’ spectra so obtained are given in Figure 6.25. The peak velocities so obtained are \(-20\) km/s for the silicon atom, \(-40\) km/s for the silicon cation and \(> 60\) km/s for the silicon dication. Clearly, the velocity of the cation scales with its charge, as was observed in the nanosecond laser ablation of graphite. Such behaviour could not be confirmed in the case of the picosecond and femtosecond laser ablation of graphite since the emission at longer distances was not intense enough to allow reliable time of flight analysis.

![Image](image_url)

Figure 6.25: The time resolved optical emission of different Si emissions. The emission was recorded in 50 \(\mu\)s time gates at 5 mm from the target surface.

A black body radiation curve was fitted to the continuum emission at wavelengths longer than 400 nm, corrected for the quantum efficiency of the spectrometer and the i-CCD array. The calculated temperature equates to 2500 \(\pm 200\) K. This temperature is above the melting temperature (1693 K) but below the normal boiling temperature (2873 K) of silicon. This would suggest that the particles giving rise to this black body radiation are molten droplets of silicon. Further evidence in support of this observation is presented in the next paragraphs.
6. Imaging of ablation plumes from KrF ablation

6.5.2. i-CCD camera images

The temporal behaviour of the total optical emission was studied in more detail by means of i-CCD images. Time resolved i-CCD camera images recorded at different delay times are shown in Figure 6.26. The pictures illustrate clearly that by 100 ns the total emission has split into at least two components.

![i-CCD images of the plume arising from femtosecond laser ablation of silicon](image)

Figure 6.26: i-CCD images of the plume arising from femtosecond laser ablation of silicon (a) after 40 ns, (b) after 160 ns and (c) after 300 ns. The spectra are recorded with a time gate of 20 ns.

This plume splitting behaviour is consistent with the observations obtained from optical emission spectroscopy. The velocity of the fast component can be estimated from cuts through the images along the surface normal. The cuts show a pronounced double peak structure on time scales above 100 ns. By taking the peak value of the fast moving component and plotting its distance from the target versus the time delay we can obtain a velocity for the fast moving component. The results of this procedure are given in Figure 6.27. The velocity so derived \(\sim 50 \text{ km/s}\) is in reasonable agreement with that deduced for the emitting Si\(^+\) from the OES measurements. Establishing a velocity for the slower component proved to be impossible because of the hot spot remaining just in front of the target.
6. Imaging of ablation plumes from KrF ablation

Figure 6.27: (a) Time of Flight transients obtained from cuts along the surface normal through the i-CCD camera images at different time delays, the slow part of the OES has been omitted from the transients. (b) The mean distance versus time plot obtained from the transients given in (a).

A yet faster emission component associated with the silicon dications, as inferred from the time resolved optical emission, is not observed in the i-CCD camera images. The fast signal obtained from the i-CCD camera images might provide a merged picture of both of the silicon cation and dication emissions.

The emission behaviour at late times was also investigated by i-CCD camera imaging. In contrast to graphite ablation, no incandescent tracks were observed but, as Figure 6.29 shows, a more continuous emission was evident in images recorded at long delay times. This variation might be connected with a difference in size and aggregation state of the ejected particles, which are assumed to be liquid droplets in the case of silicon (as opposed to solid particulates in the case of graphite).

Figure 6.28: Slow particle distribution (integration of 200 shots) of the black body radiation of the plume following the 248 nm femtosecond laser ablation of silicon, observed using a 1 µs time gate delayed by (a) 40 µs (b) 80 µs and (c) 130 µs.
The mean velocity of these emitting particles was calculated using the same method as in the case of graphite ablation. The calculated velocity along the surface normal, together with the fit to a first order exponential curve are given in Figure 6.29, along with the angular distribution. The deduced velocity is comparable to that calculated for the graphite particulates previously, although the plume is less forward directed ($n=3.1$) than in the case of femtosecond laser ablation of graphite.

![Figure 6.29: Velocity distribution of the slow particles. (a) centre of mass and (b) angular distribution for femtosecond ablation (dashed lines in (a) show the FWHM)](image)

6.5.3. Analysis of laser irradiated target material

The region of the Si target irradiated by the laser pulses was analysed by SEM imaging. Selected SEM pictures are presented in Figure 6.30. The observed surface modification in the laser spot is consistent with melting behaviour. The image shown at larger magnification on the right shows the laser interaction region in greater detail. The unablated surface shows a typical nanometer smoothness of a polished silicon wafer.
The observed surface roughness and the apparent droplet formation suggest a very violent phase transition from the liquid to the gas phase. This picture is consistent with the process of explosive boiling or phase explosion\textsuperscript{29}. Phase explosion is the process where, because of the high energy input (laser light), the melt is taken close to its critical temperature. An explosive boiling process occurs, not only at the surface but also throughout the melt, transforming the melt into a coexistent mixture of gas with molten droplets. After the phase transition, the gas phase expands into vacuum carrying the ejected droplets.

From the observed size distribution of the droplets remaining on the surface we might suggest that the average droplet size is $\sim 250$ nm. Such ejected droplets will undergo evaporative cooling and also cool via emission of black body radiation during their free flight.

### 6.6. Results and Conclusion

#### 6.6.1. Comparison of nanosecond, picosecond and femtosecond laser ablation of graphite

The optical emission from the ablation plume following nanosecond laser irradiation of graphite is visibly brighter than that from the ablation plumes resulting from pico- and femtosecond irradiation. This observation accords with the measured
removal rates (and spot size) under the different irradiation regimes. ~500 and ~100 nm/shot for the nanosecond (6.3 J/cm² / 1.8 mm²) and the femtosecond (2.1 J cm⁻² / 0.22 mm²) ablation, respectively.

The optical emission observed when using nanosecond laser pulses is distinctively different from that arising from pico- or femtosecond laser ablation: The occurrence of carbon dication emission in the latter cases indicates the higher temperature of the ejected plasma. Further there is no evidence of neutral carbon atom emission when using short pulse durations.

These observations can be explained by the different laser-material interactions that dominate when using different pulse durations. In the nanosecond case, the plasma is formed during the laser irradiation process by the interaction of the laser photons with particles ejected by the target (ions, atoms etc). The main mechanism for creating excitation and ionisation is multiphoton ionisation and inverse Bremsstrahlung in the gas phase by the laser light.

This creation mechanism cannot account for most of the optical emission observed when using picosecond and femtosecond laser pulses. The time scales of the laser irradiation in such cases are too short to obtain significant ejection of particles and hydrodynamic flow during the ablation pulse. Thus there is no justification to assign the observed optical emission to a result of the interaction of the laser light with the ablation plume. The particles must be ejected from the lattice in this highly excited and ionised state. To explain this behaviour we have investigated the models used to describe excitation and ablation processes on these time scales. Two models advanced to describe the short pulse interaction with materials are the two-temperature model and the plasma-annealing model.

The two-temperature model assumes that ablation occurs after equilibration between the lattice and the electron temperature, equating the ablation event to a fast thermal evaporation. This model cannot support the high level of ionisation observed in the plasma, since the level of ionisation is directly related to the surface temperature. Even if we assume the lower boundary of the range of plasma temperatures quoted (1.5 eV) this would equate to a surface temperature of 17000 K (calculated from conversion of eV into temperature), which is unphysically high for a solid surface.

On the other hand, the plasma-annealing model gives a reasonable explanation for the observed optical emission. In this model the high photon flux is assumed to induce a high degree of excitation in the lattice, which can be envisaged as the promotion of a
6. Imaging of ablation plumes from KrF ablation

large number of electrons into an antibonding state. This results in a very fast, electronically induced phase transition (for graphite ~90 fs\textsuperscript{16}). The resulting liquid state is closely related to a high-density plasma with a high degree of ionisation. The observed optical emission in the case of short pulse excitation is very likely to originate from a plasma formed by this creation mechanism.

Both the i-CCD camera images and the optical emission show a component attributable to C\textsubscript{2} emission just in front of the target when ablating with any of the three pulse durations. As argued in the nanosecond case, this emission probably involves a component from recombinational products of C atom collisions. The absence of C atom emission in the pico- and femtosecond laser ablation case would then suggest that there must be a significant amount of non-emitting, ground state, carbon atoms in the ablation plume available to form the dicarbon radicals. Another likely creation mechanism is the dissociative recombination of larger carbon clusters. These observations can be discussed in the framework of the two-temperature model. As mentioned previously, the two-temperature model provides a theoretical explanation for the thermal processes involved in ablation at short time-scales. After laser excitation the electron distribution energy flows into the lattice via electron-phonon coupling (typical time scale = 1-5 ps). The hot lattice will emit particles following a purely thermal mechanism, mainly in their ground state or in fast decaying excited states (governed by the Boltzmann distribution for the surface temperature). Since, for short pulse durations, this process takes place after cessation of the laser excitation, there is no interaction between the emitted particles and the laser light. These particles would thus remain in the ground state and would not be detected by optical emission.

As argued in the last two paragraphs, both of the models traditionally used to describe ablation at short time scales contribute to our understanding of the behaviour of the ejected particles. The plasma-annealing process suggests electronic excitation of the lattice, and explains the observed emission of a highly ionised plasma ball, while the two-temperature model accounts for thermal features of the ablation process.

In addition, at late time scales, a plume component is observed that is associated with ejection of large particles from the target. The temperature implied by analysis of the accompanying black body radiation indicates that the particles are solid lumps of material ejected by the target. The velocities of the ejected particles arising in both the pico- and femtosecond ablation experiments are comparable, and the velocity distribution is highly forward peaked. The velocity of the particulates exhibits an
apparent deceleration, which is explained by the underdetection of the lighter and faster, particulates at later time delays. The initial velocity ($\sim 160$ m/s) can give an estimation of the particle size of the ejected clusters $C_n (n = \sim 275)$. The plume is highly forward peaked and that can be explained as an effect of the 2D imaging of a 3D event and ejection of a microscopically rough surface. Additionally, the forward velocity of the particulates can result from the collisions of these particulates with the highly forward peaked plasma flow in the initial stages of the plume expansion.

Analysis of the deposited film showed a nanometer smooth film with a large number of incorporated carbon particles. Analysis of the ablated area on the graphite target showed evidence for local melting, consistent with arguments that a thermal mechanism (the two-temperature model) contributes to the overall ablation process. The melted surface appeared smooth, suggesting that explosive boiling does not occur during this ablation.

A last point to address is our non-observation of any suprathermal component to the cation velocity distribution. This could be due to several reasons. The suprathermal distribution is likely to consist of highly charged cations, which may have a low emission yield in the monitored wavelength range. In addition any such component would experience a lower degree of three body recombination due to its high forward velocity and consequent rapid thinning of this plasma component.

6.6.2. Comparison with the femtosecond ablation of Si(111)

The emission plume arising after femtosecond irradiation of silicon showed the same multi-component structure as observed in the case of graphite. Plasma emission was observed, from (at least) three types of emitting species, each with a well-distinguished velocity distribution. The Si$^{2+}$ ions travel with a velocity $> 60$ km/s, the silicon cations expand at $\sim 40$ km/s and the silicon atoms propagate at $\sim 20$ km/s. The observed plume splitting provides evidence for an acceleration mechanism in which the fast electrons and the cations decouple from the rest of the plume, giving rise to suprathermal velocities for the higher charged cations. The observation of such highly ionised plasma suggest that most of the underlying physics of femtosecond ablation of silicon is well described by the plasma-annealing model. In addition, a high-density region of slow moving material just in front of the target was observed. The
temperature inferred from the black body radiation emanating from this region is ~ 2500 K, indicating some contribution from a thermal mechanism i.e. the two-temperature model to the overall ablation yield.

The target also ejects large particulates as illustrated by the i-CCD camera images. These large particulates travel with a velocity of ~ 30 m/s and with a highly forward peaked velocity distribution. Such observations are consistent with the evidence for explosive boiling obtained by SEM images. The behaviour of these particles can be explained with the framework of molecular dynamics studies of the picosecond laser ablation of silicon. This latter study predicts a highly forward peaked distribution for the ejected large particles, and velocities up to 1 km/s. The apparent difference between the theoretically predicted and the experimental velocities may be attributable to the size of the calculation, since the simulation box included 32,400 atoms, which equates to a size of 5 x 5 x 27 nm. The experimental evidence hints that the ejected particles are much larger (~250 nm diameter) and consequently much slower.

The difference observed in ejection behaviour between carbon and silicon can be rationalised as follows: graphite has a much higher melting temperature and critical temperature than silicon. Silicon will thus be easier to excite to its critical temperature, thus more likely to show evidence for explosive boiling, while graphite will tend to 'cool' via fast sublimation of the solid and/or evaporation of the melt.

6.6.3. General conclusion

The optical emission from the plume arising in graphite and silicon ablation with short laser pulses exhibits a similar multi-component structure. The ejected plume consists of both non-thermal and thermal components, the non-thermal component being the ejected plasma and the thermal component consisting of large particles and very probably also non-emitting species. Both the emitting plasma and the particles exhibit a highly forward peaked velocity distribution.

These observations have important implications for film deposition with short pulse laser irradiation. For carbon, most applications require films grown with few, or preferably no embedded particulates. The results of this study indicate that the large particles could be avoided by implying an appropriate velocity filter. Deposition from femtosecond ablation has a number of disadvantages compared with the nanosecond
deposition, experimental complexity, the ablation rate is much lower, and the film quality (sp³/sp² fraction) is inferior. For silicon, on the other hand, the results suggest that laser ablation with short pulse durations might be used as a source of silicon nanoparticles.

6.7. References

6. Imaging of ablation plumes from KrF ablation

27. NIST Atomic spectra database (http://physics.nist.gov/cgi-bin/AtData/main_asd) and references therein
28. NIST Chemistry Webbook (http://webbook.nist.gov) and references therein
A1. Ablation plume properties arising from ArF PLD of aluminium and copper

The properties of plumes arising from ablation of metallic targets has been investigated briefly during this thesis work. The main reason for this study was to provide a comparison with the characteristics of carbon and ZnO ablation plumes, which were subjected to a more in depth analysis (see previous chapters). The results illustrate interesting universal properties of ablation plumes, namely their high degree of ionisation and the high kinetic energy distribution of the ions. The results also support previously introduced concepts of heating of the ablation plume by laser-plasma interaction and acceleration of the ions so created by a fast 'non-thermal' electron distribution. Study of the ablation plumes not only provides insight into the fundamental principles, but also gives a reference for the deposition of films from these ablation fluxes. The study of the ablation characteristics of aluminium and copper is a necessary prerequisite background for understanding of the production of, respectively, aluminium nitride (AlN)\textsuperscript{1} films and Cu-Co Giant Magneto-Resistant (GMR)\textsuperscript{2} films by pulsed laser deposition.

A1.1. Time integrated OES

The fluence dependence of the time integrated OES following 193 nm pulsed laser ablation of copper and aluminium in vacuum has been investigated at a distance of 5 mm from the target along the target surface normal. Spectra obtained for both species for an incident fluence of 20 J/cm\textsuperscript{2} are given in Figure 1.1.
Figure 1.1: Wavelength dispersed, time integrated OES for (a) copper and (b) aluminium monitored 5 mm from the target for a fluence of 20 J/cm². The combs identify the various emitting species within the plume. SO stands for second order. Emission line wavelengths are obtained from reference 3.

The wavelength dispersed, time integrated OES for aluminium consists of emission from neutral Al atoms, and Al⁺ and Al²⁺ cation species in the plume. The wavelength dispersed, time integrated OES for copper is much richer than the optical emission spectra for other species (e.g. Al, Zn), but all of the emission lines can still be attributed emissions from Cu neutral and Cu⁺ ionic species in the plume.

The fluence dependence of the different emitting species contained within the two plumes at a distance of 5 mm is shown in Figure 1.2. As one can see, the dependence of the signal on the fluence follows a linear relationship for the neutral atomic emission lines and a higher order relationship for the ionic emissions. The observed fluence dependence of the Al⁺ and Cu⁺ emissions can both be fitted to second order polynomial relationships, while the fluence dependence of the Al²⁺ emission is best represented by a third order polynomial fitting function. Comparing the onset fluence for creation of Cu
and Al species shows very different behaviour for the different species. The onset for Cu$^+$ emission can be approximated from the graph to be around 2.5 J/cm$^2$ while the onset for Al$^+$ and even Al$^{++}$ emission appear to be close to 0 J/cm$^2$. The Al neutral emission line, in contrast, seems to show onset behaviour but this may be more a reflection of the fact that the Al neutral lines are very weak spectral features (see Figure 1.1) and the emission intensities are close to the detection limit at low fluences.

![Graphs of fluence dependences for various emitting species](image)

Figure 1.2: Measured fluence dependences for the various different emitting species, namely: (a) Cu$^*$, (b) Cu$^{+*}$, (c) Al$^*$, (d) Al$^{+*}$ and (e) Al$^{2+*}$.

The functional form of the fluence dependent relative emission intensities of the various different species are very comparable to the curves observed for ZnO. The neutral emission is well approximated by a linear relationship, while the functional forms of the ion emissions can be fitted by higher order polynomials. These
Appendix 1: Laser ablation of Cu and Al

obsessions can be explained in terms of the formation mechanisms for the species responsible for the various emissions. As has been discussed already, at length, in former chapters, the emission arising from an atom or ion in the plume is correlated with the existence of Rydberg states of this species in the plume. More importantly, these Rydberg states are products of recombination reactions. Thus the observed $M^{n+}$ ($M =$ metal) emission is evidence for the existence of the parent $M^{(n+1)+}$ ion in the plume, and the behaviour of these emitting species closely follows the behaviour of the precursor ions in the plume. The neutral emission, which we attribute to nascent singly charged ion formation in the plume, can readily form during the ablation process by interaction of the laser light with the ejected neutrals (preferentially via MPI). Doubly (and higher) ionised species will most probably be created by interaction of the laser light with the ions (preferentially via electron-ion IBE). In this discussion it is assumed that neutral-electron IBE is negligible compared to MPI as a route to ionising the neutral atoms. The observed higher order fluence dependence of the ionic emission lines is explicable by this mechanism since IBE is a non-linear process and the density of ions created by this mechanism, and thus the amount of emission, will scale non-linearly with the fluence. The fluence onset behaviour of the Cu ion emission can than also be explained, since the IBE process needs a sufficient ion fraction in the plume to become a significant process. The Al cation emission appears not to show this threshold behaviour. This will need to be explained more carefully considering more specifically the absorption process in this material.

Comparing the ionisation potentials (IP) of the two studied materials can provide some further insight into the anomalous behaviour for Al. The ionisation energies of the Cu and Al metal atoms and ions (up to charge 4) are given in Table 1.1.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^+$</td>
<td>5.99</td>
<td>7.73</td>
</tr>
<tr>
<td>$X^{2+}$</td>
<td>24.81</td>
<td>28.02</td>
</tr>
<tr>
<td>$X^{3+}$</td>
<td>53.26</td>
<td>64.86</td>
</tr>
<tr>
<td>$X^{4+}$</td>
<td>173.25</td>
<td>122.23</td>
</tr>
</tbody>
</table>

Table 1.1: Energies (in eV) necessary to create the ions from the ground state neutral for copper and aluminium.
Important to note is that the energy to create an Al$^{+}$ ion is lower than the energy of the laser photons (ArF = 6.4 eV), while the photon energy is lower than the ionisation potential of copper. This implies that Al$^{+}$ ions can be formed by a one photon process. This is different to any of the previously studied materials, which always involved at least a two photon process to create an ion. As a consequence, an aluminium atom will be much more easily ionised by an ArF laser photon. A second consequence is that electron-ion IBE will gain in importance as an ionisation mechanism at low fluences.

A second observation that has to be explained is the occurrence of Al$^{2+}$ and Al$^{3+}$ emission lines which, we presume to correlate with the existence of Al$^{2+}$ and Al$^{3+}$ ions in the plume even at relatively low fluences. Significant Al$^{2+}$ emission is observed at an incident fluence of 2.5 J/cm$^2$, while significant Al$^{3+}$ emission is observed at a fluence of 5 J/cm$^2$. In comparison, for copper, significant Cu$^{2+}$ emission is observed at ~5 J/cm$^2$ and no Cu$^{3+}$ emission is observed. These values are derived from the absolute values of the emission intensity, taking the background noise into account. Comparing the values for the consequent IP's of both elements (Table 1.1) suggests that, although the IP values for copper are larger, the differences are not sufficient to explain the observed differences. A determining aspect of aluminium that has been identified is that Al$^{+}$ ions are created by single photon ionisation, while two photons are necessary to ionise a ground state copper atom via MPI. For the multiply charged ions, three photons are necessary to create an Al$^{2+}$ cation while 9 photons are necessary to create Al$^{3+}$ cations, the corresponding numbers for creation of Cu$^{2+}$ and Cu$^{3+}$ cations via MPI are 4 and 11, respectively. Such processes are very unlikely at the fluences used here. This also shows the predominance of electron-ion over electron-neutral IBE as a formation mechanism for the highly ionised fraction in the ablation plume.

From comparison of the time integrated, wavelength dispersed copper and aluminium OES we can conclude that aluminium has a much higher ionisation fraction than copper, over the whole studied fluence regime. Aluminium cation emission is apparent from the OES spectra even at fluences as low as 2.5 J/cm$^2$. This is attributed to a highly effective one-photon ionisation mechanism that will create aluminium cations from the ground state. From analysis of the spectra it is inferred that electron-ion inverse Bremsstrahlung is a very effective mechanism to create a fraction of multiple charged ions. A critical test for this hypothesis would involve comparison of Al and Cu ablation at longer wavelengths (e.g. 248 nm) where, in both cases, ionisation of ground state atoms would require a two photon excitation process.
A1.2. Faraday Cup measurements

TOF transients of the ion current were recorded for both copper and aluminium using the Faraday Cup assembly. The recorded TOF profiles, together with their converted velocity distributions, are given in Figure 1.3.

Figure 1.3: TOF profiles of the charged particles, measured with the Faraday Cup assembly, measured at the surface normal and a distance of 421.7 mm, and converted velocity distributions for Al ((a) - (b)), and Cu ((c) - (d)) for different fluences.

The fluence dependency of the velocity, and the kinetic energy, of the total ion yield for each species (Cu and Al) was determined from TOF profiles recorded at various incident pulse energies. Results are given in Figure 1.4. For calculating the kinetic energy, it was assumed that all detected charged particles are monatomic. This is probably a reasonable assumption given that the wavelength dispersed OES shows no evidence of any diatomic or larger emitting species (see also Chapter 4-5). Figure 1.4 presents a comparison of the mean ion kinetic energy distributions from Cu and Al ablation at 193 nm, in vacuum, as a function of incident fluence. The mean kinetic
Appendix 1: Laser ablation of Cu and Al

energy of both sets of metallic ions is higher than in the case of carbon. In addition, the mean kinetic energy of the aluminium ions is much higher than that of the copper ions. This supports the statement that laser plume heating mechanism is very effective in the case of Al ablation and is an important mechanism for coupling the energy of the laser photons with the kinetic energy of the emitted particles (in this case ions). The ionic products of the vacuum UV laser ablation of Al (at \( \lambda = 355 \text{ nm} \)) and Cu (at \( \lambda = 351 \text{ nm} \)) have been studied by both experimentally\(^4\)\(^5\) and theoretically\(^6\) by Amuruso et al. In both cases the study revealed important laser-plasma interactions at the reported wavelength, actually, the tail-off at higher fluences, also visible in Figure 1.4, has been solely attributed to laser-plasma interactions. The velocity distribution for aluminium species has been studied in more detail, via OES and Langmuir probe measurements. Results of these studies are reported in the next paragraphs.

![Figure 1.4: Fluence dependency of the velocity and the kinetic energy of the charged particles, measured with the Faraday Cup assembly, for aluminium ions ((a)-(b)) and copper ions ((c)-(d)).](image)

\(^4\)\(^5\)\(^6\)
A1.3. Time differentiated OES for aluminium

The time differentiated OES resulting from 193 nm pulsed laser ablation of Al was studied by monitoring three different emission lines at a fluence of 20 J/cm², namely the 277.6 nm line for Al⁺ neutral emission, the 335.1 nm line for Al⁺⁺ emission and the 448.0 nm line for the Al²⁺⁺ dication emission. Representative TOF transients for each of these emission lines measured at a distance of 7 cm from the target is given in Figure 1.5. This figure shows that the emitting Al⁺ neutral and Al⁺⁺ cations propagate with similar velocities while the emitting Al²⁺⁺ species propagate faster.

![Figure 1.5: TOF transients for three emission lines, measured with optical emission spectroscopy, 7 mm from the target.](image)

Velocities can be deduced from the gradient of plots of the mean (centre of the integrated) time versus observation distance. This is shown in Figure 1.6 and the resulting mean velocities are summarised in Table 1.2.
Figure 1.6: Mean velocity of emitting species in the ablation plume resulting from pulsed laser ablation of an Al target at 193 nm in vacuum, at the fluence of 20 J/cm².

<table>
<thead>
<tr>
<th>Species</th>
<th>Velocity (km/s)</th>
</tr>
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<tbody>
<tr>
<td>Al⁺</td>
<td>28.7 ± 0.6</td>
</tr>
<tr>
<td>Al²⁺</td>
<td>27.3 ± 1.3</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>40.9 ± 0.9</td>
</tr>
</tbody>
</table>

Table 1.2: Mean velocity of the three components of the emission deduced from the time versus distance plots such as those shown in Figure 1.5.

The TOF-OES data indicate that the nascent Al⁺ and Al²⁺ ions (monitored via Al⁺ and Al²⁺ emissions) propagate with similar velocities while the Al³⁺ ions (Al²⁺ emission) propagate ~50 % faster. It is notable that the time versus distance plots are not particularly straight lines, especially for the case of Al⁺ emissions; indeed, there is an indication of a curvature, which could be correlated with acceleration for all three species. This behaviour is comparable to the observations reported for the Zn⁺ emission from ZnO (Chapter 5).

Also noticeable that none of the mean velocities determined from the OES measurements for an incident fluence of 20 J/cm² are as high as the mean ion velocity determined by the Faraday Cup measurements. To further investigate this apparent
A1.4. Langmuir Probe transients for aluminium

The electron current from the ablation plume arising from the 193 nm ablation of aluminium in vacuum has also been studied, using the Langmuir probe assembly. The TOF transients recorded with the Langmuir probe positioned 3 cm from the target along the target surface normal are shown in Figure 1.7. The TOF profiles show a fluence dependent double peak behaviour. The early time peak in the TOF transient increases in intensity relative to the later peak as the incident fluence is increased.

Figure 1.7: TOF transients recorded with the Langmuir probes at 3 cm from the target, the applied fluences are (a) 5 J/cm$^2$, (b) 10 J/cm$^2$, (c) 15 J/cm$^2$ and (d) 20 J/cm$^2$. The spectra are taken with a 2 μs delay time.

The mean velocity can be deduced from the TOF transients: and the results are summarised in Table 1.3.
<table>
<thead>
<tr>
<th>Fluence (J/cm²)</th>
<th>Velocity (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>21.0 ± 0.8</td>
</tr>
<tr>
<td>10</td>
<td>26.7 ± 0.4</td>
</tr>
<tr>
<td>15</td>
<td>27.9 ± 0.1</td>
</tr>
<tr>
<td>20</td>
<td>28.8 ± 0.4</td>
</tr>
</tbody>
</table>

Table 1.3: The mean velocity of the electrons monitored by a Langmuir Probe positioned 3 cm from the Al target, as a function of fluence.

The mean velocity of the distribution rises as a consequence of the higher fraction of the fast component, but the mean velocity of the total electron signal is still slower with that of the ions derived from the Faraday Cup transients. To investigate the possibility of an acceleration of the ions and electrons (like in references 7-9), the electron current was also measured at a distance of 7 cm from the target and at the fluence of 20 J/cm². The obtained TOF is given in Figure 1.8 with its conversion into a velocity distribution.

![Figure 1.8: Velocity distribution of the electrons, measured by a LP at a distance of 7 cm from the target, for 193 nm Al ablation at a fluence of 20 J/cm².](image)

A1.6. References

The derived mean velocity is 36.5 ± 0.5 km/s, significantly larger than the mean velocity derived at the distance of 3 cm, but still smaller than the ion velocity derived from the Faraday Cup transients. The recorded data suggest that both the electrons and the ions in the ablation plume undergo significant acceleration during their flight through vacuum. The acceleration is believed to have the same origin as the acceleration observed in ZnO, namely a hot 'non-thermal' electron distribution, which induces a bipolar expansion in the plume.

A1.5. Conclusion

The ablation of copper and aluminium at 193 nm, in vacuum, using focused nanosecond laser pulses was briefly studied. The OES spectra showed the presence of highly ionised plumes, and the ionisation could be attributed to combined effects of MPI and IBE. The higher degree of ionisation in the Al ablation plume is likely due to the fact that one ArF laser photon carries sufficient energy to ionise all neutral Al atoms, even in the ground state. Faraday Cup measurements revealed that the ionic component of the plumes propagate with very high kinetic energies (~ 200 eV for Cu and ~ 300 eV for Al). The development of such high kinetic energies has been investigated in the case of Al ablation via time resolved OES and Langmuir probe studies also. The Langmuir probes reveal the presence of a non-thermal electron component, which accelerates the plume, as in the case of ZnO (Chapter 5). Comparison between the Langmuir probes and the Faraday Cup measurements reveal an additional 40% increase in centre of mass expansion velocity of the ions as the plume expands from 30 to 421.7 mm from the target.

A1.6. References

Appendix 1: Laser ablation of Cu and Al

3 NIST Atomic spectra database (http://physics.nist.gov/cgi-bin/AtData/main_asd) and references therein


A2. Operation of the Quadrupole Mass Spectrometer

A large part of this PhD work has been involved with optimising a state of the art Quadrupole Mass Spectrometer (HIDEN, HAS-5PL-4353). This Mass Spectrometer has been developed for plasma analysis sources and is conveniently called an Electrostatic Quadrupole Plasma Probe or EQP. The EQP can be used in two operating modes, the Residual Gas Analysis (RGA) mode to record spectra of neutral species in the plasma and the Secondary Ions Mass Spectrometry (SIMS) mode to record spectra of ionised species in the plasma. As stated in Chapter 2 the mass spectrometer can be divided into five regions, which will be discussed in technical detail.

A2.1. Detailed Description of the Apparatus

A detailed figure of the Mass Spectrometer with its associated electrostatic lenses is given in Figure 2.1. The entrance pinhole has a chosen diameter of 2 mm. This diameter of pinhole was necessary in order to obtain a good signal to noise for the spectra because the plume is typically sampled at ~275 mm from the target.

Highly important for understanding the operation of the EQP is a detailed knowledge of its electrical circuitry. The lenses are set at defined potentials by several independent power supplies. These independent power supplies are connected to each other as illustrated in Figure 2.2. An understanding of the operation of each power supply and the effect of a set voltage on the connected electrodes is essential for understanding the operation of the EQP.
Appendix 2: Operation of the QMS

Figure 2.1: Detailed figure of the Mass Spectrometer with its associated electrostatic lenses (ESA = Electrostatic Analyser, QMF = Quadrupole Mass Filter, SEM = Secondary Electron Multiplier). The components in blue are adjusted to our specific needs.

Figure 2.2: Circuit diagram showing the various bias voltages and their connections within the Hiden mass spectrometer.
For example, scanning energy scans not only the voltage on axis but also on lens2, focus2, transit-energy, suppressor and 1st dynode. When changing any voltage care must be taken to assess which other voltages will change and the effect they will have.

The reference power supply allows detection of particles with energy ≤ 1100 eV. For example, by setting this voltage at 200 V, every other electrode is also set at 200 V plus their respective individual power supply voltage. Energy can only scan between -100 and +100 eV. In order to scan an energy range of 0-300 eV, two separate scans will be needed. Longer scans in energy space are possible by scanning reference but, in doing so, extractor and lens1 are also scanned, which is unfavourable.

Many of the voltages displayed in Figure 2.2 are determined by the manufacturer and seldom need to be changed. The machine specific values for these voltages are determined when the instrument was initially tuned. The voltages on all of the electrodes are crucial if the apparatus is to be operated correctly, and it is important to discuss the specifics of these lenses. The apparatus can be divided into five separate regions, as previously discussed:

**The extraction region**

The extraction region exists of two electrostatic lenses, the extractor and lens1. The extraction region is very important when measuring ion currents in SIMS mode. A more detailed discussion of the influence of these two lenses on the transmission of the ions through the EQP is given later in this Appendix. When recording ion spectra the voltage on these lenses was set to 0 V (or -reference, see earlier discussion) since the ions in this study are clearly travelling with non thermal velocities (e.g., for the ablation of graphite, at up to 200 eV). The extraction region is of lesser importance for the detection of neutral particles (RGA mode) in the ablation plume, since they are not affected by the voltages on these lenses. In RGA mode, the extraction region can be used to repel accompanying ions in the plume.

**The source region**

The source region is important when recording spectra in RGA mode, since this is the region where ions are created from neutrals via electron bombardment. The electron source comprises two tungsten filaments which can be both switched on at the same
time. The electrons are accelerated in the cage for ionisation. In standard mode both of the filaments are set to an emission current of 1000 mA and the electron acceleration voltage is set to 30 V. The cage can be set on a positive voltage to accelerate thermal species without flow velocity, into the mass spectrometer. In the present work, however, this voltage has been set to 0 V since the ablation plume is expected to exhibit a centre of mass velocity distribution. The neutral distribution has been proposed to have a 2-3 times smaller mean velocity than the ions in a standard ablation experiment. Thus the mean centre of mass kinetic energy of the neutral species in our ablation plume is not expected to be higher than 10 eV. The ionised neutral species are subsequently focused at the beginning of the field free region. The optimal value for the voltage on the source focus in our experiments was found to be -67 V. From the connection diagram (Figure 2.2) it is obvious that in SIMS mode the source region is set on the same potential as the field free region and simply acts as an extension to the field free region.

The electrostatic analysis region

The electrostatic analysis region exists of a field free region with a quadrupole energy filter positioned behind it. Kinetic energy selection is obtained since the ions transit through the field free region with an energy which is equal to the sum of the axis voltage and the energy voltage. Since the axis voltage is typically -20 V, the particles with an initial energy equal to the energy potential will have a kinetic energy of 20 eV after the field free region. The Electrostatic Analyser (ESA) is tuned so as to transmit only particles with a kinetic energy towards the detection region equal to the axis potential. Lens2 focuses the ions into the ESA for energy filtering (the voltage is typically set to 20 V). The ESA is a 45° sector field energy analyser which is controlled by plates, vert, horiz, D.C. quad and axis. The D.C. quad region is tuned up via an iterative procedure to optimise the signal.

The advantage of locating the ESA before the quadrupole mass filter, as compared with other experimental QMS or TOF set-ups, is that it is then not necessary to make any assumptions about the residence time within the mass filter, which can critically influence such measurements. The residence time in a normal QMS set-up has to be known since the energy of the particles are measured via their TOF profile after mass.
selection. With thermal species ($< kT$) this residence time can be assumed constant, but for high kinetic energy particles the residence time becomes a complicated function of both its mass and energy.

**The quadrupole mass filter**

After kinetic energy selection by the ESA, the ions are decelerated and focused by focus2 before injection into the quadrupole mass filter (QMF). The QMF consists of a main filter driven by RF and DC, with a pre- and post-filter driven by RF only. **Transit energy** is a virtual voltage source which allows the energy for the ion transit through the QMF to be explicitly set (typical voltage: 3V).

**The detection region**

The detector is an ion counting secondary electron multiplier (SEM) which is mounted off-axis. 1stDynode sets the voltage on the front of the detector.

During our work with the mass spectrometer a number of modifications have been introduced in an attempt to meet the specific needs imposed by studying a plasma generated by laser ablation (shown in blue in Figure 2.1). One important adjustment was the introduction of a small diode laser to enable precise alignment of the mass spectrometer axis to the ablation spot. Also, additional pinholes have been introduced in an effort to ensure transmission of only those particles that are almost solely forward directed, i.e. with minimal off-axis velocity component. The source region was also rebuilt to enhance the ionisation cross-section. This was necessary because of the low density of the ablation plume at the detection distance.

**A2.2. Specific usage of the EQP in Laser Ablation**

Since pulsed laser ablation is a time gated event, the EQP has to be used in time gated mode also. The triggering and time gate arrangement normally used is illustrated in Figure 2.3. This set-up also ensures a high signal to noise ratio. The acquisition time
for a single point on an energy scan ranged between 5-25 ms which, given the 0.5 ms
time gate used, means that every point on an energy spectrum is an accumulation of 10-
50 shots. This set-up obviously leads to very long acquisition times (for example
recording 400 points at 25 ms acquisition times equates to > 30 minutes ablation time)
and, as discussed in Chapter 2 such time scales are too long to perform in a single
ablation run. The solution to this problem is to record a complete spectrum in several
separate ablation runs, or to record a spectrum with a smaller number (~ 50) of points.

Figure 2.3: Time gating of the mass spectrometer

The (x,y) translation stage is used to provide a fresh target surface when recording
the spectra. This method worked well in most circumstances although some
considerations when operating with the (x,y) translation stage have to be taken into
account. Firstly, the area through which the target can be rotated is fully exposed in ~30
minutes, precluding experiments that extend beyond this period. Second, the ablation
yield can be very sensitive to the surface morphology, so high surface uniformity is
desirable. To this end, it is best to work with a mirror polished target sample, and to
gently pre-ablate the entire surface area of interest prior to the mass spectrometer
investigation. There are situations where the earlier rotating target design is preferable,
e.g. when performing near-threshold ablation studies (where signal levels are
necessarily small), since the (x,y) translation stage introduces a higher degree of
contamination into the vacuum.

To counter this latter problem a purpose built cold finger can be attached to the
laser ablation chamber when performing low fluence studies. This consists of a copper
rod inserted in the vacuum and in contact with liquid nitrogen through a stainless steel
Appendix 2: Operation of the QMS

The design is shown in Figure 2.4. The contamination of the vacuum is reduced by applying this cold finger, resulting in a $\sim 10\times$ reduction in the base pressure of the vacuum chamber.

![Diagram of cold finger design](image)

Figure 2.4: Cold finger design.

A2.3. Experimental Determination of the System Performance

The experimental determination of the system performance has to deal with two questions. First of all, does the apparatus provide a well-calibrated energy scale? If this requirement is met the second question is whether the energy dependent transmission function is a smooth curve, ideally a straight line with gradient of 0. As shown in Chapters 3-5 this is a critical requirement, especially in laser ablation applications since the ion kinetic energy can have a very broad distribution stretching from 0 eV till hundreds of eV. This behaviour is quite unique to ablation generated plasmas in vacuum and will impose some severe demands on the detection apparatus. The neutral fragment distribution is expected to be much narrower and to have a lower mean kinetic energy ($< 10$ eV). The different restrictions for the two operational modes, RGA and SIMS mode, are discussed in the following paragraphs.
A2.3.1. RGA mode

The validity of the energy scale and the energy dependence of the transmission function in RGA mode can be assessed experimentally by applying a voltage to the cage electrode while monitoring the energy distribution of a residual gas in high vacuum (in our case N\textsubscript{2} in $5 \times 10^{-8}$ Torr). Sample results are shown in Figure 2.5. The maximum cage voltage is 10 V so the apparatus can only be calibrated for particle kinetic energies $\leq 10$ V, which is probably sufficient for the present application.

![Figure 2.5: Determination of the energy scale and the transmission function in RGA mode](image)

Figure 2.5: Determination of the energy scale and the transmission function in RGA mode, the cage voltage has been varied from 3 to 10 V so as to accelerate the ions generated within the source region towards the TOF tube. Assuming a thermal velocity for these generated ions, the voltage on the cage will accelerate them to a terminal velocity of a maximal value (in eV) of cage voltage.

Not only the energy scale is in good accordance with the expected values, but also the transmission function appears to be relatively independent of the kinetic energy. This analysis suggests that the monitoring of the neutral particles and their kinetic energy distribution in the ablation plasma is valid within the 0-10 eV region.
A2.3.2. SIMS mode

A calibrated ion source producing high kinetic energy ions is necessary for the calibration of the ion energy scale in SIMS mode. A suitable Cs⁺ ion source was provided by HIDEN. It consists of an ion generation region comprising a piece of Cs containing glass (Kimball) heated by two filaments. The ions are initially accelerated in a focusing optic (Bessel box) and are further accelerated to yield ion kinetic energies in the range of 30-100 eV. The energy calibration in SIMS mode, shown in Figure 2.6, reveals an excellent agreement between the ion energies calculated from the known accelerating potentials and those recorded by the mass spectrometer.

![Figure 2.6: (a) Recorded mass spectrum of Cs⁺ ions, and (b) energy calibration in SIMS mode.](image)

Unfortunately, the transmission function cannot be deconvoluted from this experiment. A comparison between the kinetic energy distributions of C⁺ ions resulting from graphite ablation in vacuum measured using the Faraday Cup and with the Mass spectrometer is shown in Figure 2.7. Clearly, these reveal huge differences. The transmission function thus appears to be highly dependent on the kinetic energy of the particles.
Figure 2.7: Comparison of the kinetic energy distributions of C\(^+\) ions from 193 nm ablation of graphite in vacuum as recorded by (a) mass spectrometer and (b) Faraday Cup for a fluence of 2.5 J/cm\(^2\).

The first attempt to overcome the problem of deconvoluting the transmission function was a purely experimental approach, involving tuning of voltages on the extractor and lens 1 ion optics so as to ensure maximum transmission for every energy. For this approach the kinetic energy spectrum was taken in chunks ranging from a few eV to a few tens of eV and the settings for the voltages on the lens 1 and extractor electrodes were optimised for every kinetic energy region. The resulting spectra for C\(^+\) and C\(^{2+}\) ions are shown in Figure 2.8.
Figure 2.8: Mass spectrometer measurements of the ionic components in the ablation plume following 193 nm irradiation of graphite at a fluence of 20 J/cm². The C⁺ signal was monitored at m/q = 12 and the C²⁺ was monitored at m/q = 6. The extractor lens and lens 1 were tuned up for different energy regions to obtain maximal transmission for the whole energy range.

Clearly this procedure yields a much smoother kinetic energy distribution, but it is still not in accord with the Faraday Cup spectra. The main reason for this is the incorrect assumption that the mass spectrometer, even if tuned up, will necessarily have the same transmission for particles with different kinetic energies. A more detailed discussion about the reasons underlying the inherent kinetic energy dependent transmission function of the apparatus is given below.

A2.4. Modelling of the Transmission Function with SIMION

The transmission of ions through the mass spectrometer has only been modelled for the SIMS mode of operation since the transmission of these particles through the mass spectrometer seem to show the greatest kinetic energy dependence. As discussed in section A2.1, all the ions transmitted through the ESA and into the QMS will have the same kinetic energy (axis potential). Thus the transmission function beyond the field free region should only be mass and not kinetic energy dependent. Thus only the front region of the mass spectrometer, up till the ESA in Figure 2.1, needs to be considered.
when investigating the kinetic energy dependent transmission function for a given ion mass/charge ratio. A model of the front part of the mass spectrometer has been provided by Hiden in the form of a SIMION potential array file and the SIMION software has been used to study the trajectories of ions in these electric fields and thus the energy dependent transmission. For the calculations we have concentrated on the transmission function of singly charged carbon cations (m/q = 12).

The first study we have performed is to model and compare the energy dependent transmission behaviour of the mass spectrometer when ions enter with either only a forward velocity component or with both forward and radial velocity components, a small angle of ± 4° was chosen. For these calculations the voltages on the lens1 and extractor ion optics were set to 0 V, and the potential on the ionisation region and axis was set to (−20 V + Energy (see Figure 2.2)), to resemble closely the standard experimental conditions. The results, shown in Figure 2.9, reveal that in both of the cases the transmission function is far from an ideal smooth horizontal line. The experimental curve shown in Figure 2.8 bears more resemblance to the case where the ion beam has a radial velocity component. This is consistent with the experimental observations reported in Chapters 4 and 6. In the further discussion only calculations with a ± 4° angular spread will be considered.

![Figure 2.9: Calculated transmission function for (red) 0° and (black) ±4° angular spread of the incoming ions, for energies of 0-100 eV.](image-url)
These transmission functions have been obtained by calculating the trajectory of 50,000 individual ions for every calculated kinetic energy with a spread of initial directions (given by an angular value defined relative to the instrument axis), and by changing the radius of the ion incidence relative to the centre of the mass spectrometer by a given distance. The transmission efficiency for every radius has to be multiplied by the circumference of the circle, since we are modelling a 2-D slice from a 3-D situation. These calculations are quite time demanding and inefficient. For these reasons, a Monte Carlo add-in program was implemented in the SIMION software that allowed randomised selection of the initial angle and radius of the incident ion. With this Monte Carlo routine, we could reduce the number of ions per run drastically, normally 1000 ions per run was used to produce qualitatively the same result as the non-Monte Carlo result.

The reason for the dramatic energy dependence of the transmission function was identified as, primarily the region between lens 1 and the source region (maintained at axis + energy potential, see section A2.1). Indeed, when the electric field gradient is plotted out in the SIMION image a kinetic energy dependent electric field is observable between lens 1 and the source region, which acts as a lens (see Figure 2.10). This lens has a energy dependent focusing effect as can be observed from the trajectories of ions of different kinetic energies. The focal point for different kinetic energies can be deduced from the calculations and figures for different kinetic energy ions are given in Table 2.1 (also consider Figure 2.10 for comparison of the focal lengths).

<table>
<thead>
<tr>
<th>Energy ion (eV)</th>
<th>Focal point (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>67</td>
</tr>
<tr>
<td>10</td>
<td>162</td>
</tr>
<tr>
<td>20</td>
<td>$\infty$</td>
</tr>
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<tr>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>100</td>
<td>62</td>
</tr>
</tbody>
</table>

Table 2.1: The distance of the focal point, calculated from the extractor entrance for different kinetic energies. Only particles with angular spread of $\pm 0^\circ$ were used in the trajectory calculations. The figures can be compared with the red curve in Figure 2.8.
Appendix 2: Operation of the QMS

The figures in Table 2.1, show that the focal point of this kinetic energy dependent lens is highly affected by the kinetic energy of particles (or the Axis-Energy potential). This lensing effect is depicted as the main reason for the large kinetic energy dependency of the transmission function.

Figure 2.10: Detailed image of the energy selection region of the mass spectrometer (before the ESA), with dimensions. The region in light blue shows the energy dependent electric field.

A second point we have to address is the accuracy of the SIMION calculations and the agreement between such simulations and experiment. Figure 2.11 compares calculations for two different settings of the axis potential (20 and 40 V) with experimental spectra recorded with the mass spectrometer under the same conditions. It is important to recognise that the experimental data is a convolution of the carbon ion kinetic energy distribution and the transmission function, so the curves can not be directly compared with each other. Nevertheless, the calculated curves show qualitative accord with the experimental data, in agreement with the notion that the experimental curve is in fact a much smoother energy dependent function (as implied by the Faraday Cup measurements).
Figure 2.11: Experimental spectra (a) and (b) taken with the mass spectrometer in SIMS mode for carbon ions (m/q = 12) with the standard voltages on the lenses (0 V on extractor and lens 1) and, (a) 20 V and (b) 40 V for the axis voltage and a ± 4° angular spread. Theoretical spectra obtained from SIMION calculations for the same voltage settings on the lenses and with a voltage of (a) 20 V and (b) 40 V on the axis.

Unfortunately, the calculated curves cannot be used for any quantitative assessment of the kinetic energy dependent transmission function. The main reason for this is that the SIMION calculations consider a set of non-interacting ions, which is a poor representation of the reality. The optics focus the ions to a focal point the position of which is kinetic energy dependent (see Table 2.1). It is highly unlikely that particles with the same kinetic energy will not interact in these focii (where the mean distance between the particles is the smallest). SIMION has an option of including allowance for repulsion between ions but a correct value for the interaction cannot be given since this value is dependent on the ion density -which is the property we are trying to deconvolute! Thus this is an ill-defined problem. The SIMION results, even neglecting inter-ion repulsion, can nevertheless still be validated as predictor values to gain insight into the behaviour of the mass spectrometer.
A2.5. Experimentally Determined Transmission Function

If we assume that the Faraday Cup signal is the true kinetic energy dependent ion distribution then we can deconvolute the mass spectrometer transmission function. The resulting deconvolution gives a transmission function in terms of a 9th order polynomial with the expression:

\[ y = A + B_1 E + B_2 E^2 + B_3 E^3 + \ldots + B_9 E^9 \]

where \( E \) stands for the energy (in eV). Representative figures for the coefficients are given in Table 2.2. This set of figures are for the mass spectrometer operating in SIMS mode and for the following voltages on the lenses in the front of the mass spectrometer: 0 V on extractor and lens 1, and -20 V for the axis potential. Since the transmission function is expressed as an energy dependent function, it is assumed to be mass and charge independent. This transmission function is fitted in between a kinetic energy window of 0-200 eV, and it does not represent the transmission function at higher kinetic energies.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
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<tbody>
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</tr>
<tr>
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<td>( B_9 )</td>
<td>6.6159E-18</td>
</tr>
</tbody>
</table>

Table 2.2: The values for the different coefficients for the 9th-order polynomial fit for the following conditions: extractor and lens 1 at 0 V and axis at 20 V.
Additionally, we have also studied the cases of putting a small attracting and repelling voltage (± 5 V) on the ion optic lens I next to a large attracting voltage (-50 V) to obtain information about correction for the large differences in the kinetic energy dependent transmission function. The results of the calculations are given in Figure 2.12. Different voltages on lens I yield different transmission functions, which is expected. None of the transmission functions seem to be smoother than the original transmission function (0 V on lens I), showing that applying voltages on the ion optic lens I will not greatly improve the energy dependence of the transmission of the mass spectrometer.

Figure 2.12: Calculated transmission function for different voltages on lens 1, (a) –5 V, (b) –50 V, (c) 0 V and (d) 5 V.

A2.6. Conclusion

The performance of a state of the art QMS specifically built for analysis of ablation plumes has been investigated. The conclusion of the performance can be divided in 2 parts.
Appendix 2: Operation of the QMS

1. For detecting neutral atoms in RGA mode, the mass spectrometer operates adequately. As derived from experimental data, the transmission function is not dependent on the kinetic energy of the particles (in between 3-10 eV) and the improved source region enables detection of neutral species in low density ablation plumes.

2. In SIMS mode, for detection of ions, the mass spectrometer exhibits a detrimental in-built flaw. Because of its construction it has a highly kinetic energy dependent transmission function. This problem can only be solved by reconstruction of the front end of the mass spectrometer, e.g. by introducing a set of highly transmitting grids in between the ion optics lens 1 and source region. This will deplete the electric field curvature between those two optics, which will enhance the transmission function.

Throughout this thesis it has been shown that the ionic species within the ablation plume are easily detected with a number of other techniques (e.g. OES, Faraday Cup, Langmuir probes), while information about the atomic species is much more difficult to access. Since the strength of this QMS lies in the detection of neutral species, studying the atomic species within the plume with this system can add to the understanding of the ablation process.

A2.7. References


3 SIMION 3D. Scientific Instruments Services, version 6.
A3. Linelist for neutral carbon atoms

Details of transitions of Cl observed during the PLA of graphite and CVD diamond:

**Carbon (CI):**

Ground state: $1s^2 2s^2 2p^2, 3p^0$

Ionisation Potential: 11.269 eV

<table>
<thead>
<tr>
<th>State'</th>
<th>State''</th>
<th>$E^\prime$ (eV)</th>
<th>$E''$ (eV)</th>
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<td>7.49</td>
<td>909.5</td>
</tr>
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<td>$^1S;3p$</td>
<td>$^1P^0;3s$</td>
<td>9.17</td>
<td>7.68</td>
<td>833.4</td>
</tr>
<tr>
<td>$^3P^0;5s/4d$</td>
<td>$^3D;3p$</td>
<td>10.38</td>
<td>8.64</td>
<td>711.8</td>
</tr>
<tr>
<td>$^1P^0;4d$</td>
<td>$^1P;3p$</td>
<td>10.42</td>
<td>8.54</td>
<td>658.7</td>
</tr>
<tr>
<td>$^3F^0;5d/6s$</td>
<td>$^3D;3p$</td>
<td>10.71</td>
<td>8.65</td>
<td>601.7</td>
</tr>
<tr>
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<td>7.95</td>
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<td>$^1P;3p$</td>
<td>10.72</td>
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<tr>
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<td>$^1P^0;3s$</td>
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<td>7.68</td>
<td>538.1</td>
</tr>
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<td>$^1P^0;3s$</td>
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<td>7.68</td>
<td>505.2</td>
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<td>$^3P^0;3s$</td>
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<td>7.49</td>
<td>477.0</td>
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<td>$^3P^0;3s$</td>
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<td>$^1P^0;3s$</td>
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<td>10.81</td>
<td>396.9</td>
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<td>$^1P^0;3s$</td>
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<td>$^1S;2p^3$</td>
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<td>2.68</td>
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<tr>
<td>$^3P^0;3s$</td>
<td>$^1S;2p^3$</td>
<td>7.68</td>
<td>1.26</td>
<td>193.0 ♦</td>
</tr>
</tbody>
</table>

♦ Emission observed in 2nd order transmission through monochromator.

A4. Linelist for carbon cations

Details of transitions of CII observed during the PLA of graphite and CVD diamond.¹

**Carbon (CII):**

*Ground state: 1s² 2s² 2p¹ 3P⁰₁/₂*

<table>
<thead>
<tr>
<th>State'</th>
<th>State''</th>
<th>E' (eV)</th>
<th>E'' (eV)</th>
<th>Observed Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴P;3p</td>
<td>⁴P⁰;3d</td>
<td>24.65</td>
<td>23.12</td>
<td>807.7</td>
</tr>
<tr>
<td>⁴P;3p</td>
<td>⁴P⁰;3d</td>
<td>24.65</td>
<td>23.12</td>
<td>806.2</td>
</tr>
<tr>
<td>⁴P;3p</td>
<td>⁴P⁰;3d</td>
<td>24.65</td>
<td>23.11</td>
<td>804.7</td>
</tr>
<tr>
<td>⁴D;3d</td>
<td>⁴P⁰;3p</td>
<td>18.05</td>
<td>16.33</td>
<td>723.5</td>
</tr>
<tr>
<td>⁴D;3d</td>
<td>⁴P⁰;3p</td>
<td>18.05</td>
<td>16.33</td>
<td>723.5</td>
</tr>
<tr>
<td>⁴P;3d</td>
<td>⁴D;3p</td>
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<td>22.54</td>
<td>711.8</td>
</tr>
<tr>
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<td>⁴P⁰;3d</td>
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<td>22.90</td>
<td>706.4</td>
</tr>
<tr>
<td>⁴S;3p</td>
<td>⁴P⁰;3d</td>
<td>24.66</td>
<td>22.90</td>
<td>704.6</td>
</tr>
<tr>
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<td>⁴P⁰;3s</td>
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</tr>
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<td>²S;3s</td>
<td>16.33</td>
<td>14.45</td>
<td>658.2</td>
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<td>²F⁰;4f</td>
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<td>20.95</td>
<td>646.1</td>
</tr>
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<td>²D;4d</td>
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<td>20.84</td>
<td>615.1</td>
</tr>
<tr>
<td>²D⁰;3d</td>
<td>²P;3p</td>
<td>24.60</td>
<td>22.57</td>
<td>610.0</td>
</tr>
<tr>
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<td>²D;3d</td>
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<td>18.05</td>
<td>589.4</td>
</tr>
<tr>
<td>²P;3s</td>
<td>²S;3p</td>
<td>22.90</td>
<td>20.71</td>
<td>566.2</td>
</tr>
<tr>
<td>²P⁰;3s</td>
<td>²S;3p</td>
<td>22.90</td>
<td>20.71</td>
<td>564.8</td>
</tr>
<tr>
<td>²D;4p</td>
<td>²P⁰;3d</td>
<td>26.63</td>
<td>24.27</td>
<td>526.0</td>
</tr>
<tr>
<td>²P;3p</td>
<td>²P⁰;3s</td>
<td>23.12</td>
<td>20.71</td>
<td>514.6</td>
</tr>
<tr>
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<td>²F⁰;3d</td>
<td>27.48</td>
<td>24.79</td>
<td>462.0</td>
</tr>
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<td>²D⁰;3d</td>
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<td>24.60</td>
<td>441.2</td>
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<td>24.65</td>
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<td>²P;3p</td>
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<td>23.11</td>
<td>432.2</td>
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<tr>
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<td>²D;3d</td>
<td>20.95</td>
<td>18.05</td>
<td>426.8</td>
</tr>
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<td>²D⁰;3d</td>
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<td>24.37</td>
<td>407.7</td>
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<td>²D⁰;3d</td>
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<td>24.37</td>
<td>397.0</td>
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<tr>
<td>²S;4s</td>
<td>²P⁰;3p</td>
<td>19.49</td>
<td>16.33</td>
<td>392.2</td>
</tr>
<tr>
<td>(^2\text{G};4f)</td>
<td>(^4\text{F}^{2};3\text{d})</td>
<td>27.47</td>
<td>24.27</td>
<td>387.3</td>
</tr>
<tr>
<td>(^2\text{D};3\text{p})</td>
<td>(^2\text{P}^{2};4\text{p})</td>
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<td>383.7</td>
</tr>
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<td>(^4\text{P}^{0};4\text{s})</td>
<td>(^4\text{D};3\text{p})</td>
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<td>22.53</td>
<td>359.1</td>
</tr>
<tr>
<td>(^3\text{P}^{0};5\text{p})</td>
<td>(^3\text{D};3\text{d})</td>
<td>21.73</td>
<td>18.05</td>
<td>336.3</td>
</tr>
<tr>
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<td>(^2\text{D}^{0};2\text{p}^{3})</td>
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<td>18.65</td>
<td>316.8</td>
</tr>
<tr>
<td>(^2\text{F}^{0};5\text{f})</td>
<td>(^3\text{D};3\text{d})</td>
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<td>299.3</td>
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<td>(^2\text{S}^{2};2\text{p}^{2})</td>
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<td>(^3\text{D};4\text{d})</td>
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<td>16.33</td>
<td>274.7</td>
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<tr>
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<td>(^4\text{D};3\text{p})</td>
<td>27.22</td>
<td>22.54</td>
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<tr>
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<td>(^2\text{P};2\text{p}^{2})</td>
<td>18.65</td>
<td>13.72</td>
<td>250.8</td>
</tr>
</tbody>
</table>

* Emission observed in 2\(^{nd}\) order transmission through monochromator.

A5. Linelist for carbon dications

Details of transitions of CIII observed during the PLA of graphite and CVD diamond.¹

Carbon (CIII):

<table>
<thead>
<tr>
<th>State'</th>
<th>State''</th>
<th>$E'$ (eV)</th>
<th>$E''$ (eV)</th>
<th>Observed Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3P^o,3p$</td>
<td>$^3S,3s$</td>
<td>32.19</td>
<td>29.53</td>
<td>464.7</td>
</tr>
<tr>
<td>$^1D,2p^2$</td>
<td>$^1P^o,2s2p$</td>
<td>18.09</td>
<td>12.69</td>
<td>229.7*</td>
</tr>
</tbody>
</table>

* Emission observed in 2⁰ order transmission through monochromator.

### A6. Linelist for zinc atoms and cations

Details of transitions of ZnI observed during the PLA of ZnO

**Zinc (ZnI):**

- **Ground state:** $^1S$
- **Ionisation Potential:** 9.39 eV

<table>
<thead>
<tr>
<th>Transition</th>
<th>$E'$ (eV)</th>
<th>$E''$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>Observed wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3P \rightarrow ^3D$</td>
<td>4.01</td>
<td>7.78</td>
<td>3.78</td>
<td>328.16</td>
</tr>
<tr>
<td>$^3P \rightarrow ^3D$</td>
<td>4.03</td>
<td>7.78</td>
<td>3.75</td>
<td>330.36</td>
</tr>
<tr>
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<td>4.08</td>
<td>7.78</td>
<td>3.71</td>
<td>334.37</td>
</tr>
<tr>
<td>$^3P_0 \rightarrow ^3S_1$</td>
<td>4.01</td>
<td>6.65</td>
<td>2.65</td>
<td>468.14</td>
</tr>
<tr>
<td>$^3P_1 \rightarrow ^3S_0$</td>
<td>4.03</td>
<td>6.65</td>
<td>2.63</td>
<td>472.31</td>
</tr>
<tr>
<td>$^3P_2 \rightarrow ^3S_1$</td>
<td>4.08</td>
<td>6.65</td>
<td>2.58</td>
<td>480.94</td>
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<td>$^1P \rightarrow ^1D$</td>
<td>5.80</td>
<td>7.74</td>
<td>1.95</td>
<td>636.30</td>
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<tr>
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<td>4.01</td>
<td>8.50</td>
<td>4.50</td>
<td>275.65</td>
</tr>
<tr>
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<td>4.02</td>
<td>8.50</td>
<td>4.47</td>
<td>277.10</td>
</tr>
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<td>4.01</td>
<td>8.11</td>
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<td>8.11</td>
<td>4.04</td>
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<td>4.03</td>
<td>4.03</td>
<td>307.59</td>
</tr>
</tbody>
</table>
Appendix 6: ZnI and ZnII linelist

Details of transitions of ZnII observed during the PLA of ZnO

**Zinc (ZnII):**

**Ground state:** $^2S_{1/2}$

**Ionisation Potential:** 27.36 eV

<table>
<thead>
<tr>
<th>Transition</th>
<th>$E'$ (eV)</th>
<th>$E''$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>Observed wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2S_{1/2} - ^2P_{1/2}$</td>
<td>6.01</td>
<td>10.96</td>
<td>4.95</td>
<td>250.20</td>
</tr>
<tr>
<td>$^2S_{1/2} - ^2P_{3/2}$</td>
<td>6.12</td>
<td>10.96</td>
<td>4.85</td>
<td>255.80</td>
</tr>
<tr>
<td>$^2D_{3/2} - ^2F_{3/2}$</td>
<td>12.02</td>
<td>14.54</td>
<td>2.52</td>
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</tr>
<tr>
<td>$^2D_{3/2} - ^2F_{7/2}^{5/2}$</td>
<td>12.02</td>
<td>14.54</td>
<td>2.52</td>
<td>492.40</td>
</tr>
<tr>
<td>N/A</td>
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<td>2.10</td>
<td>589.43</td>
</tr>
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<td>$^2D_{5/2} - ^2P_{1/2}$</td>
<td>12.57</td>
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</tr>
<tr>
<td>$^2D_{5/2} - ^2P_{1/2}$</td>
<td>14.63</td>
<td>15.90</td>
<td>1.27</td>
<td>610.25</td>
</tr>
<tr>
<td>N/A</td>
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<td></td>
<td>1.66</td>
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<td>$^2P_{3/2} - ^2S_{1/2}$</td>
<td>10.96</td>
<td>12.57</td>
<td>1.60</td>
<td>758.85</td>
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<tr>
<td>$^2S_{1/2} - ^2P_{3/2}$</td>
<td>12.57</td>
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<tr>
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<td>12.60</td>
<td>1.63</td>
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<td>12.60</td>
<td>14.20</td>
<td>1.60</td>
<td>775.79</td>
</tr>
</tbody>
</table>

1 NIST Atomic spectra database (http://physics.nist.gov/cgi-bin/AtData/main_asd) and references therein