Optical studies of micron-sized particles immersed in a plasma

Citation for published version (APA):

DOI:
10.6100/IR528213

Document status and date:
Published: 01/01/1999

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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This work is part of the research programme of the 'Stichting voor Fundamenteel Onderzoek der Materie (FOM)', which is financially supported by the 'Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)'.

Ontwerp omslag: B. Mobach

Drukwerk: Universiteitsdrukkerij Technische Universiteit Eindhoven

CIP-DATA LIBRARY TECHNISCHE UNIVERSITEIT EINDHOVEN

Swinkels, Gerardus Hubertus Petrus Maria

Dit proefschrift is goedgekeurd door de promotoren:

prof.dr. F.J. de Hoog
en
prof.dr. H. Deutsch

Copromotor:
dr.ir. G.M.W. Kroesen
Contents

1. Introduction .................................................................................................................. 1
   1.1 Dusty plasmas in the semiconductor industry ......................................................... 1
   1.2 Coulomb crystallization ........................................................................................... 4
   1.3 Dust utilization ........................................................................................................ 7
   1.4 Scope of this thesis .................................................................................................. 9

2. The interaction between plasma and dust ................................................................. 11
   2.1 Charging .................................................................................................................. 11
   2.2 Forces ..................................................................................................................... 13
   2.3 Strongly coupled plasmas ....................................................................................... 15

3. The interaction between light and dust ................................................................. 17
   3.1 Mie theory ............................................................................................................. 17
   3.2 Stokes vectors and Mueller matrices ..................................................................... 22

4. Dust particles monitored with a rotating compensator ellipsometer ......................... 27
   4.1 Introduction ............................................................................................................. 27
   4.2 RCE theory ............................................................................................................ 27
   4.3 Experimental Setup ............................................................................................... 30
   4.4 Results ................................................................................................................... 31
   4.5 Conclusions .......................................................................................................... 40

5. Mueller Matrix Ellipsometry ...................................................................................... 41
   5.1 Introduction ............................................................................................................. 41
   5.2 Historical perspective of the GEC cell .................................................................... 41
   5.3 Experimental setup ............................................................................................... 42
   5.4 Theoretical background on the Mueller Matrix Ellipsometer ................................. 44
   5.5 The calibration of the optical system ...................................................................... 47
   5.6 Results ................................................................................................................... 49
     5.6.1 Accuracy ......................................................................................................... 50
     5.6.2 Single particles in the discharge ...................................................................... 53
     5.6.3 Dust clouds in the discharge .......................................................................... 59
   5.7 Conclusions .......................................................................................................... 63

6. Forward scattering on a single particle ....................................................................... 65
   6.1 Introduction ............................................................................................................. 65
   6.2 Setup .................................................................................................................... 66
   6.3 Simulations ............................................................................................................ 67
   6.4 Measurements ....................................................................................................... 69
   6.5 Conclusions .......................................................................................................... 78

7. The thermal balance ................................................................................................. 81
   7.1 Introduction ............................................................................................................. 81
   7.2 Setup .................................................................................................................... 81
   7.3 Gas temperature measurements .......................................................................... 87
     7.3.1 Theory ............................................................................................................. 87
1. Introduction

1.1 Dusty plasmas in the semiconductor industry

In the eighties, contamination of semiconductor surfaces caused by dust particles was recognized as a very serious problem for the semiconductor industry. This contamination influenced device topography, performance, reliability, and as a result also manufacturing yield was reduced [1]. Therefore, all fabrication steps were moved to clean rooms in which the particle contamination levels could be controlled and monitored. Furthermore, several other polluting processes like wafer handling and material flaking of the chamber walls were identified and corrected by improved procedures for chamber cleaning and maintenance.

However, in spite of all these and several other precautions, chemical sources of particulate contamination remained present in the processing environment: the semiconductor processing plasmas themselves appeared to be a serious source of dust particulate production [1 - 3]. A very schematic picture of a plasma is given in Fig. 1.1.

\[\text{Figure 1.1: A schematic view of a radio-frequency plasma. The plasma is created between two electrodes and consists of different constituents; neutrals (molecules or atoms), electrons, and positively charged ions are always present, sometimes also radicals, negatively charged ions, and dust particles can be found. In the plasma, two regions can be distinguished: the glow (a bright region), and two electrical boundaries known as sheaths (no light emission).}\]

The plasma is struck between two planar conducting electrodes, one of which is grounded. To the other one a sinusoidal voltage (13.56 MHz) is applied. As a result the electrons move in this time-varying electromagnetic field, whereas the ions are not able to
follow the field. The mobility of the electrons is much larger than the mobility of the electrons, as is their average velocity. This can lead to a charge separation, which in turn generates an electric field. As a result, in the glow, the diffusion of electrons and ions is coupled, and this is known as ambipolar diffusion. Due to the high mobility of the electrons, everything that is brought into contact with a plasma is charged negatively. This leads to a loss of the electrons to e.g. the walls. Instantaneously, a strong electric field builds up all around the glow that repels the electrons from the walls and it accelerates the ions towards the walls. Now a second region in the plasma can be distinguished: the sheath. The glow is a bright region; the energetic electrons in the glow collide with neutral species, which results in light emission. The sheath is a dark region since the density of the electrons rapidly decreases to zero. Besides electrons and ions, several reactive species might be present in the plasma.

Due to the nature of the plasma, particulates in its volume obtain a negative charge and therefore are trapped in the discharge; in Fig. 1.2 an illustrative example of dust trapping in a radio-frequency (RF) argon plasma is shown.

**Figure 1.2:** Particles trapped in a 20 Pa, 5 W argon RF plasma struck in a Gaseous Electronics Conference (GEC) Reference Cell. On the electrode a small aluminum ring is present to modify the trapping conditions. Therefore particles are located only in the center of the plasma.

As a result of the identification of plasmas as a particulate source an extensive, worldwide research effort [1, 3 - 8] was started, initiated by the semiconductor community to understand particle nucleation, growth, and trapping with the intention to avoid or to reduce particle contamination. It turned out that in the most common surface processing plasmas formation of dust particles roughly took place in two general situations:

1. **The dust is created by surface phenomena.**

During the plasma treatment of surfaces, e.g. etching of silicon wafers with CCl$_2$F$_2$/Ar a small-scale roughness is created on the surface [9 - 11]. This roughness or micro-mask can be caused by local oxidation or contamination, and is etched at a lower rate than the surrounding silicon wafer; it might even not be etched at all. A passivation layer is deposited on the sidewall of the micro-mask, which creates a column. Finally the micro-mask is etched away, and then the interior is etched out. Only the passivation sidewall remains, standing freely. A hollow column results, which ultimately breaks off. The column has a negative charge and is injected into the glow by the electrostatic field. By
deposition of e.g. CF$_2$ radicals it can grow further [9]. These etching plasmas are used in the semiconductor industry in the manufacturing process of integrated circuits (IC’s). Formation of dust is extremely unpleasant; one single dust particle, if it has the same size as the trenches of the device, can destroy a complete IC. The modern development towards ever increasing structure density leads to a size reduction of the structures, and as a consequence even smaller particles can become ‘killer particles’ [11].

Another possibility is that the surface supplies the chemical species that initiates particle growth. An example of this is argon sputtering of graphite electrodes [12], where the sputtered carbon forms the dust. The condensation kinetics of carbon are much faster than any of other element [13], and the clustering reactions lead to dust formation.

2. The dust is created due to gas phase phenomena

The plasma itself has a strong tendency to generate the particles. Examples of these dust-forming plasmas are the well-known silane (SiH$_4$) and other polymerizing plasma chemistries [5, 10, 14 - 17]. These plasmas are used in PECVD applications (Plasma Enhanced Chemical Vapor Deposition) like thin film deposition of e.g. solar cells, flat panel displays and thin film transistors. A major problem is that the unwanted dust formation occurs in the situation where the highest deposition rates are achieved. Dust formation and subsequent deposition can lead to a deterioration of the film quality.

The formation of the dust particles in the gas phase proceeds in three steps:

a) The negative ions that are trapped in the plasma glow become large negative ions due to the recombination with silane radicals. The electronegativity of these large ions reduces and the total charge starts to fluctuate; the cluster is alternatively charged positively, negatively, and sometimes it is neutral.

b) The clusters coalesce; the fluctuation of the charge prevents the clusters to repel one another.

c) The clusters have become so large that a permanent negative charge builds up; the repulsive force prevents further growing of the particle due to coalescence. No new nucleation is possible because the particles collect almost all the free electrons; sometimes the particles are ‘coughed out’ by the plasma and a new generation of dust particles can nucleate. In this third phase the particles slowly grow by surface deposition of amorphous silicon (which is an example of PECVD) [7].

Coming to this understanding of the whole nucleation and growth process of dust particles in silane plasmas was possible with the results of several diagnostics that helped in unraveling the mechanism. In step (a) both mass spectrometry and photo-detachment in combination with microwave cavity resonance measurements evidenced the presence of the negative ions. The mass spectrometry results showed that negative ions grow too much higher mass numbers than the positive ions. It is believed that this phenomenon is the basis of the particle nucleation in radio-frequency silane plasmas. The photo-detachment measurements indirectly evidence the fluctuation of the cluster charge; the average charge of the clusters is 0.1.

In step (b) the particle size has been measured in situ with Mie scattering and ex situ with transmission electron microscopy (TEM); the Mie scattering also gives information on the number density. The size increases, while the density decreases rapidly. In the last step (c), the build-up of the constant negative charge on the clusters is followed with microwave cavity resonance measurements. The deposition of amorphous silicon on the particles is monitored with time-resolved infrared absorption. With this diagnostic the different absorption bands in a silane plasma are recorded; the measurements indicate that the Si-H absorption only becomes strong if the coagulation phase is finished and deposition of amorphous silicon takes place. Furthermore, the size of the particles with respect to the wavelength of the light is such that the particles scatter according to the Rayleigh law; this can be seen in the infrared absorption spectrum [7].
As a result of the understanding of the formation mechanism of dust, practical solutions can be devised to diminish their deposition on the wafers. One innovation has been suggested and applied by Selwyn [18]. He proposed a grooved electrode, which acts as a potential well for the particles. The particles gather in there, and subsequently are transported to the pump port. This leads to a drastic improvement in process performance.

Other solutions are the ramping of the RF power and the modulation of the plasma. With the first technique the plasma is not switched off abruptly, but more ‘sensibly.’ Dust trapping becomes less efficient, and the particles are allowed to leak out before the plasma is switched off. Modulating the plasma only works if the duty cycle and the modulation frequency are chosen properly; one has to make sure that the plasma-off time is such that the negative ions (clusters) can leave the plasma. Then it is impossible for the dust to grow. A disadvantage of this technique is that the plasma has to be switched on again. Every time this happens a breakdown voltage is present that might damage the device.

Although the presence of dust in plasmas has been regarded as a nuisance, it also has its benefits. These will be treated in the next two chapters.

### 1.2 Coulomb crystallization

In addition to powder formation, also artificially injected powders in plasmas have become an important area of research. In the plasma, the particles acquire a negative charge and thus are trapped. Depending on the particle size, trapping occurs at different positions in the plasma, this is shown in Fig. 1.3.

![Figure 1.3: Schematic representation of particle trapping in the plasma; the particles are represented by the gray area. Case (a) indicates large particles (several microns) for which gravity is one of the dominant forces. As a result the particles will float in layers above the bottom electrode. Case (b) indicates small particles feeling the drag force of the ion wind near the sheath edges that concentrates the particles in layers close to both electrodes. Case (c) is for even smaller particles (0.1 micron) that are not subjected to gravity or ion wind and they will float all over the plasma glow. Case (d) is a schematic picture of 15 µm diameter particles under microgravity conditions during a rocket flight; in the center a spheroidal void is created where no particles can be seen [19]; case (d) is also noticed in plasmas on earth [20]. It is suggested [21] that these voids result from a balance of electrostatic and ion drag forces.](image-url)

To determine the trapping position of the particles it is important to realize that all the particles in the plasma are subjected to several forces. These will be treated in more detail in chapter 2. An important force for large particles (several microns) is the gravitational force. This is shown in Fig. 1.3, case (a): the gravitational force pulls the particles to the
bottom electrode and the electric field in the sheath tries to push the particles back to the glow. Therefore large particles will be trapped in the sheath of the bottom electrode.

The electrical field in the sheath repels the dust particles, but accelerates positive charged ions. These ions exert a frictional force on the particles and drag the particles towards the electrodes. This happens in case (b). Particles, which have a size in the order of 1 micron, are located in layers close to both the electrodes. Even smaller particles, 100 nm’s, can be located everywhere as they do not feel the gravitational force and the ion drag; this is shown in case (c).

The gravitational force is an important force, and therefore experiments under microgravity conditions are very interesting, see case (d). Results of rocket flights indicate that the particles, which have a diameter of 15 µm, are located all over the plasma glow. However, in the centre of the glow a spheroidal ‘void’ is created. This void is a particle free region, suggested to be created by the thermophoretic force [19]. These voids are also seen in dusty plasmas that are investigated in the laboratory [20]. In these voids, the electron density is increased due to the absence of ‘electron-consuming’ dust particles. It is observed that the void has a distinct and sharp boundary, resulting in a complete dust free region inside the void and a finite value for the dust density outside the void. Furthermore, it has been shown that voids in both laboratory and microgravity plasmas can result from a balance of the electrostatic and ion drag forces on a dust particle, where the particle size and the electric field strength determine a threshold for the void [21].

The particles in the plasma are not only subjected to forces created by the plasma environment, but due to their large negative charge the particles interact mutually via their Coulomb forces. Ikezi [22] theoretically predicted that dust particles in plasmas could create Coulomb lattices if the Coulomb energy exceeds the kinetic energy of the particles. Some years ago Coulomb crystals were found in several systems:

- Thomas et al. [23] observed a Coulomb crystal after the artificial injection of 7 µm spheres in a 200 Pa, 4.5 W argon radio-frequency discharge. The particles were observed to be organized in 18 planar layers parallel to the electrode. An increase of the radio-frequency power led to an increase of the particle kinetic energy and as a result the particle cloud became liquid-like.
- Hayashi et al. [24, 25] grew carbon particles in a 40 Pa, 10 W methane plasma; a liquid-to-solid phase transition occurred when the particles became larger than 1.3 µm; a hexagonal crystal structure has been identified after the phase transition.
- Chu et al. [26, 27] grew 10 µm SiO2 particles in a 40 Pa, 100 W SiH4/O2/Ar radio-frequency discharge. They observed hexagonal, fcc, and bcc structures.

In Fig. 1.4 a black-white inverted image of a Coulomb crystal is shown. The crystal consists of 10 µm diameter polymer particles that were injected into an argon radio frequency discharge. The image was taken during a stay at the DLR (Deutsches Zentrum für Luft- und Raumfahrt, Institut für Raumsimulation, Cologne, Germany) on the GEC reactor of Thomas. To create the Coulomb crystal it is necessary to inject the particles into the plasma. Therefore a ‘saltshaker’ is used that is mounted on a manipulator arm. In the plasma the particles acquire a negative charge and are trapped in the sheath. To prevent that the particles are flushed away, a ring is located on the electrode that modifies the electric potential and enhances the particle trapping. Furthermore, very low gas flow rates are used.

In order to visualize the particles a HeNe laser has been used. The light beam of the laser is directed through a cylindrical lens and the beam is transformed into a sheet. A CCD camera and a video recorder are used to record the behavior of the particles as a function of radio-frequency power, gas pressure, gas species, particle size, dust density,
ring size, ring shape, etcetera. Afterwards the videotape is used for a detailed analysis of the behavior of the Coulomb crystal.

Coulomb crystals are very interesting and excellent ‘model systems’ for the study of several solid state processes like phase transitions, self-organization, thermodynamical properties, and lattice defects. Furthermore insight might be gained into several basic plasma process, like plasma-dust interaction, dust acoustic waves, and the dust particles might act as microprobe to reveal information on the local behavior of the plasma chemistry. Besides the Coulomb crystal, several other solid state model systems exist [28]:

- Soap bubble systems and Langmuir-Blodgett films have been used for the investigation of lattice defects and melting transitions respectively. These systems are two-dimensional systems and phase transitions are hard to reproduce.
- Electron solids have been found in semiconductor materials like GaAs – AlGaAs heterojunctions. These solids are hard to observe directly.
- Colloidal crystals (2D and 3D) can form in aqueous environments. These systems have very long settling times. Furthermore, colloidal crystals are produced with monodisperse particles with sizes of a few hundred nanometers. This hampers the detection.
- Ion crystals can be created in Paul and Penning traps. As with the electron solids these crystals are hard to observe.

**Figure 1.4:** A black-white inverted image of a Coulomb crystal; the melamine formaldehyde particles (black dots) have a diameter of 10 µm and are trapped in an argon radio-frequency discharge. The size distribution of the particles is very narrow and as a result all particles are trapped at the same height in the plasma. The collective effects induced by Coulomb repulsion lead to the formation of the crystal. This image is taken with a CCD camera. To visualize the particles a HeNe laser has been used, and the laser beam is transformed into a sheet with the aid of a cylindrical lens.

Compared with other model systems, the Coulomb crystal is a very interesting model system because of its unique properties [28]:

- The crystal is easy to produce and to reproduce; standard laboratory equipment suffices for the creation of Coulomb crystals, and with straightforward
diagnostics an enormous amount of information on the behavior of the crystal can be gathered.

- The crystal can be controlled very easily: reversal of parameter changes, like rf power and gas pressure results in a return to the old situation.
- The crystal can be visualized with a HeNe laser and can be observed with the naked eye since micron-sized particles can be used to create the plasma.
- The plasma crystal has a fast response time, and thus reacts directly to changes in e.g. the rf power.

All these properties have made the Coulomb crystal a very interesting subject of investigation. In the last years, research applied to the Coulomb crystal has uncovered a lot of information [19, 23, 28 - 33]. More information has been gained by monitoring the gas-liquid-solid phase transitions, several new wave phenomena have been discovered, lattice vibrations and vibrations of single particles have been investigated revealing charging properties of particles. The increased knowledge can be used to answer several solid state problems like the origin of defects, but it can also be used to improve the dusty plasma research on the application side.

1.3 Dust utilization

The increased knowledge and the ability to control the particles in the plasma has recently led to new lines of research. In the past, dust production in radio-frequency discharges was unwanted because of its deleterious effects on surfaces. Nowadays, the production of dust in radio-frequency discharges is no longer undesirable. Particles can be produced with unique and desired qualities and this opens up new possibilities for their use in several applications like ceramics, catalysis, and also optoelectronics. In the following, some examples of the different applications will be given [5, 34].

**Optoelectronics.** Some years ago, experimental evidence was given that nanometer sized structures of silicon material are able to emit photons in the visible spectrum at higher energies than the natural bandgap of bulk material. Among others, plasma technologies have been devoted to the synthesis of such systems, which have very promising optoelectronic and electronic properties. Furthermore, these nanostructured layers can have interesting mechanical properties like hardness and elastic modulus.

Roca i Cabarrocas [35, 36] devoted research to the deposition of these layers. He and his co-workers deposited plasma produced nanometer-sized silicon particles onto a silicon surface, while coating the surface with an amorphous silicon layer. The incorporation of these particles into the layer led to an enhancement of the layer properties: the crystalline character of the layer was improved, it had a higher stability under thermal annealing, and the defect density reduced. As a result, this material is very promising for thin film transistors and solar cells: the microcrystalline films have a higher mobility, an improved doping efficiency and a better long-term stability than the amorphous silicon films that were deposited.

The incorporation of nanocrystallites into an amorphous matrix can also be done with other materials. Silicon nanocrystallites have been deposited on a substrate (e.g. glass), interchanged with the deposition of transparent materials (Si$_3$N$_4$), and this resulted in composite films, which show photoluminescence [7]. Others have seeded TiN nanocrystals in Si$_3$N$_4$ layers that can obtain a hardness of 5\,10$^6$ N/mm$^2$ and an elastic modulus of 50 GPa.
Ceramics, catalysis and protection. In several plasma reactors it is possible to mix different feed gases. Adding methane, ammonia and nitrogen to silane plasmas leads to the formation of dust particles, which are based on these gases. A good control of reactor temperature and gas flow allows creating a desired particle stoichiometry. With the mentioned feed gases, particles like Si$_3$N$_4$ and SiC have been formed. Both materials are shown to have very good mechanical and thermal properties, and thus are excellent catalyst support powders [37, 38]. Furthermore, the particles are dense, stable and are resistant against oxidation.

Vivet [38] has grown ceramic powders in a methane-silane plasma. In a successive step a Pd wire has been inserted into the plasma, where it was sputtered. The palladium vapor condensed on the particles; the palladium formed speckles (‘islands’ or cauliflower structures) on the particle surface. This is the ideal morphology for catalytic applications: the speckles increase the total active area of the catalyst. Kersten [34] has used another technique to coat particles. He applied a magnetron sputter gun to coat particles in a radio frequency discharge. The discharge is used only as a trapping and separation device for the particles that are injected from the outside. The injected iron powder particles were coated with a thin, closed, aluminum layer. The coated particles had a rough and cauliflower-like shape, which makes them attractive, especially for catalytic applications.

Furthermore, it is pointed out that treating the particles can enhance the optical, mechanical, thermal, electrical and magnetic properties of the particles. Unfortunately the magnetron sputtering has a low efficiency, 30% of the particles are coated, and a low throughput (up to 1 mg per run of 10 minutes). For future industrial applications it is necessary to process a significantly larger amount of powder; this of course depends on reactor size, coating speed, process homogeneity, etc.

Figure 1.5: SEM photograph of a MoS$_2$ sample obtained in a discharge fed with MoCl$_5$ vapor, H$_2$S and H$_2$ [39]. The particles are produced in ten subsequent runs; during collection they started to stick together.

Stoffels et al. [39] investigated the formation of MoS$_2$ in a radio-frequency discharge. These particles are very interesting because of their lubricating properties; embedding them in a hard coating of e.g. titanium nitride results in a self-lubricating hard coating. To form the particles, MoCl$_5$ is thermally evaporated and an argon stream flushes the vapor to the discharge. There the vapor is mixed with H$_2$S and H$_2$ in the discharge. In Fig. 1.5 a sample of the produced material is shown. With this method, it is possible to obtain a
monodisperse size distribution of the particles, with a desired mean size smaller than 100 nm. Hydrogen is added to the discharge because it enhances the stability and the purity of the particles. At the moment, it is necessary to switch between the different chemistries in order to deposit the titanium nitride layers after the production of the particles has been finished.

In the future, more methods will be developed to benefit from particle formation, growth, trapping, and treatment in a discharge. In laboratory plasmas the processed powders have very promising features. Hopefully, the problems met in the past like coating efficiency, processing yield will be solved in the near future.

1.4 Scope of this thesis

This thesis deals with optical studies performed on micrometer-sized dust particles floating in radio-frequency discharges in argon and oxygen.

In chapter 2 the interaction of plasma and dust particles is treated. In the plasma the particles acquire a negative charge and furthermore they are subjected to several forces. These forces cause trapping of the particles in the radio-frequency discharge and can lead to the formation of Coulomb crystals.

Chapter 3 is concerned with the interaction of light and the particles. In this chapter the famous Mie theory is introduced that is needed to relate scattered light to particle properties. To describe the transport of polarized light in an optical system and its interaction with objects under investigation, some vector algebra is introduced. This mathematical description of light is done with the help of Mueller matrices and Stokes vectors.

In chapter 4 the etching of a cloud of particles in an oxygen discharge is monitored with a rotating compensator ellipsometer (RCE) that is constructed around an aluminum test reactor. This RCE can be described with the previously introduced Mueller matrices and Stokes vectors. The diagnostic is developed to determine in situ the particle sizes while particles are being treated in a radio-frequency plasma.

The difficulties met with the rotating compensator ellipsometer can be solved by using another, more sophisticated ellipsometer. This enhanced ellipsometer, the Mueller matrix ellipsometer (MME), is introduced in chapter 5. It has been used for the same purpose as the RCE, namely to monitor clouds of particles during their trapping in plasmas. It has also been used to monitor single particles trapped in the plasma. The MME is capable of measuring the full Mueller matrix, and as a result the particle shape can be monitored. The experiments have been performed in a commercial system. This reactor, the Gaseous Electronics Conference (GEC) RF reference cell, will be treated in more detail in this chapter.

The scattering signature of a single particle trapped in an oxygen discharge has been monitored during oxygen treatment; this is the subject of chapter 6. The forward scattering signal of the particle, illuminated with an argon-ion laser is recorded. This method has been developed to determine the particle size in an accurate way. It will be demonstrated that this diagnostic, together with its numerical routines is capable to determine a varying particle size.

The particles in the plasma are charged negatively due to the electrons. The negatively charged particle attracts positive ions that are incident on its surface. On the particle surface, recombination takes place of these incident ions with the electrons and subsequently energy will be deposited onto the particle. This influences the internal
temperature of the particle. This temperature is measured with the help of dyed particles; the fluorescent emission of the particles is shown to be temperature dependent. The thermal balance can describe the change of the internal particle temperature; this is done in chapter 7. In this context it was necessary to determine the gas temperature and plasma parameters like electron density and electron temperature.
2. The interaction between plasma and dust

In this chapter the theoretical background behind electrostatic interactions between plasma and dust are treated. A particle in a plasma acquires a charge. This charge is determined by the equilibrium of ion and electron currents to the particle. A simple charging theory is the orbital motion limited (OML) theory that will be treated in this chapter. Furthermore several forces work on the particle and their magnitudes determine whether or not the particle will be trapped.

2.1 Charging

Due to their higher mobility electrons move faster than ions and therefore objects suspended in a plasma will be charged negatively; photoemission and secondary electron emission do not play an important role. This negative charge subsequently gives rise to an acceleration of the ions towards the floating object, and thus to an ion current; the resulting diffusion of both species is known as ambipolar diffusion. In a steady state, the electron current and the ion current toward the floating object will be equal. A well-known, relatively simple, and often applied charging theory for particles is the ‘orbital motion limited’ theory (OML) [40, 41]. This theory was developed to describe the charging of spherical or cylindrical Langmuir probes. With these metallic conductors a current is drawn in the plasma and a $I - V$ characteristic is determined. From this $I - V$ characteristic plasma parameters like electron and ion density as well as electron temperature can be determined. This can also be reversed: when the plasma density and temperatures are known it is possible to determine the current.

In the OML theory an isolated particle with radius $r_p$ is assumed to fulfil $r_p << \lambda_D << \lambda_{mfp}$, with $\lambda_D$ the electron Debye length and $\lambda_{mfp}$ the collisional mean free path between neutral gas atoms and either electrons or ions [42]. The ions and electrons moving towards the particle are coming from infinity and global plasma parameters are attained. An ion with an energy $E_i$ is attracted by the particle and will gain an energy $e \phi$ ($\phi<0$) in the field of the particle; see Fig. 2.1. Conservation of energy and angular momentum holds [33].

![Figure 2.1: The trajectory of an ion in the central field of a negative charged particle with radius $r_p$. The ion has an impact parameter $b$ which is smaller than the critical impact parameter $b_c$. The potential of the particle is $\phi<0$ where the plasma potential is the reference.](image)

Using these two conservation laws a critical impact parameter $b_c$ can be calculated
\[ b_i = r_p \sqrt{1 - \frac{e\phi}{E_i}}, \]  

(2.1)

and a cross section for ion capture can be defined

\[ \sigma_c = \pi b_i^2 = \pi r_p^2 \left(1 - \frac{e\phi}{E_i}\right). \]  

(2.2)

Now it is possible to determine the ion current to the particle assuming a Maxwellian energy distribution of the ions

\[ I_i = n_i e \pi r_p^2 \int_0^\infty \left(1 - \frac{e\phi}{E_i}\right) \sqrt{\frac{2E_i}{m_i}} \exp\left(-\frac{E_i}{k_B T_i} - \frac{2\pi}{(\pi k_B T_i)^{1/2}} \sqrt{E_i} \exp(-E_i/k_B T_i) dE_i, \]  

(2.3)

where \( T_i \) is the ion temperature, \( m_i \) is the ion mass and \( n_i \) is the ion density. Integration finally yields

\[ I_i = n_i e \pi r_p^2 \left(1 - \frac{e\phi}{k_B T_i}\right) \sqrt{\frac{8k_B T_i}{\pi m_i}}, \]  

(2.4)

where the particle has a potential \( \phi < 0 \). In the same manner the electron current can be determined. However, the electrons need to overcome the potential barrier \( e\phi \) and thus only electrons with a higher energy will reach the particle; the other electrons will be deflected. This yields an electron current equal to

\[ I_e = -n_e e \pi r_p^2 \sqrt{\frac{8k_B T_e}{\pi m_e}} \exp\left(-\frac{e\phi}{k_B T_e}\right), \]  

(2.5)

where \( T_e \) is the electron temperature, \( m_e \) the electron mass, and \( n_e \) the electron density.

The ion and electron current determine the charge of an isolated particle; in a steady state the charge \( Q \) does not change under influence of these currents. This implies that

\[ \frac{\partial Q}{\partial t} = I_i + I_e = 0. \]  

(2.6)

Influenced by the currents the potential of the particle will be altered in order to obtain this steady state situation; this potential is known as the floating potential \( \phi_f \). The particle charge can be found by solving the current balance:

\[ 1 - \frac{e\phi_f}{k_B T_i} = \frac{m_i T_e n_e e}{m_e T_i n_i} \exp\left(\frac{e\phi_f}{k_B T_e}\right). \]  

(2.7)

Note that this equation is independent of the particle radius \( r_p \). The charge \( Q \) on a particle can be found from \( Q = C\phi_f \) where the capacity \( C \) of the particle is assumed to be equal to \( C = 4\pi \varepsilon_0 r_p \). Equation (2.7) is solved and the results are shown in Table 2.1: the floating
potential and the number of charges $Z$ are determined for a single isolated particle of 5 µm radius immersed in argon.

Table 2.1: Steady state solution of the floating potential and the number of charges, $Z$, for a 5 µm particle in an argon plasma.

<table>
<thead>
<tr>
<th>$T_e$ (eV)</th>
<th>$T_i$ (eV)</th>
<th>$\phi_f$ (V)</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03</td>
<td>-2.806</td>
<td>-9700</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>-3.058</td>
<td>-10600</td>
</tr>
<tr>
<td>3</td>
<td>0.06</td>
<td>-3.058</td>
<td>-27700</td>
</tr>
</tbody>
</table>

### 2.2 Forces

Particles immersed in RF plasmas are subjected to several forces. The forces differ in magnitude and thus of importance.

**Gravity**

A particle in the plasma is subjected to gravity:

$$F_g = m_p g = \frac{4}{3} \pi r_p^3 \rho_p g,$$

where $m_p$ the particle mass, $\rho_p$ the mass density of the particle, $g$ the gravitational constant, and $r_p$ the particle radius. Gravity pulls the particles towards the lower electrode; larger particles are pulled harder due to the third power dependence on the particle radius.

**Electric force**

The electric force pushes the particles from the electrodes:

$$F_E = QE,$$

and it is very important because it is responsible for the trapping of the particles in the discharge. In the glow of the plasma, the electric field is much smaller compared to the electric field in the sheath. The charge $Q=C \phi_f$ may be found by requiring charge conservation on the particle, Eq. (2.7). The capacitance $C=4 \pi \varepsilon_0 r_p$ depends linearly on the particle size; the floating potential $\phi_f$ does not depend on particle size but is determined by the plasma parameters.

**Ion drag**

From the plasma-sheath edge the ions are accelerated towards the electrode. This directed ion flux causes a momentum transfer from the positive ions to the particles. The induced force [43] is known as the ion drag force

$$F_{id} = K_{id} n_i m_i \vec{v}_{i,rel},$$
where \( n_i, m_i, \) and \( v_{i,rel} \) are the positive ion density, mass, and the average velocity with respect to the particles. \( K_{mt} \) is the momentum-transfer rate coefficient and can be calculated from

\[
K_{mt} = \int_0^\infty \sigma(v_i) v_i f(v_i) dv_i, \tag{2.11}
\]

where \( \sigma(v_i) \) the ion momentum cross section and \( f(v_i) \) the ion speed distribution function. The cross section can be approximated by

\[
\sigma(v_i) = c_1 b_0^2 \ln(1 + c_2 \frac{\lambda^2}{b_0^2}), \tag{2.12}
\]

which was the result from a screened Coulomb potential profile and classical scattering theory. Here \( c_1 = 0.94, \ c_2 = 61, \ b_0 = (2e^2 Z_p)/(4\pi\varepsilon_0 m_i v_i^2) \) is the collision parameter for deflection at 90º (\( Z_p \) is the number of elementary charges), and \( \lambda \) is the mean free path length. [10]

**Neutral dr.**

Like the momentum transfer from positive ions, also the neutral gas particles can transfer their momentum to the particles. This force is known as the neutral drag force and it is given by

\[
\vec{F}_{nd} = \frac{4}{3} \pi r_p^2 n_n m_n v_{th}(\vec{v}_{th} - \vec{v}_n), \tag{2.13}
\]

where \( n_n, m_n, \) and \( v_{th} = \sqrt{8k_B T_n / \pi m_n} \) are the neutral density, mass, and the thermal speed of the neutral particle; \( T_n \) is the neutral temperature. \( (\vec{v}_j - \vec{v}_p) \) is the relative velocity of particle and the flow velocity of the neutrals [17]. The neutral drag force is only present when the particle has a different speed with respect to the neutral gas; in this case the particle is hit more on the front than on the backside. This results in a deceleration of the particle speed.

This representation of the neutral drag force is only valid if the particle size is much smaller than the mean free path of the neutrals. In that case the particle does not influence the velocity distribution of the neutrals, which is true for most cases of our interest.

**Thermophoresis**

A temperature gradient in the plasma causes a particle movement to colder parts of the plasma. Neutrals from a hotter area have a higher velocity, and can thus transfer more momentum to the particles than cold neutrals. This causes a net force in the direction of the colder parts of the plasma. The thermophoretic force is given by

\[
\vec{F}_{th} = -\frac{32}{15} r_p^2 k_{trans} \frac{\nabla T_n}{v_{th,n}} \tag{2.14}
\]

where \( k_{trans} \) is the translational part of the thermal conductivity of the gas [44].
2.3 Strongly coupled plasmas

As above-mentioned, the electrical force and the gravitational force play an important role in the trapping of negatively charged particles in a plasma. If the particle density is very high collective effects start to play a role, and the possibility exists that a Coulomb crystal is formed. Therefore it is necessary that the plasma is ‘strongly coupled’, i.e. Coulomb collisions are frequent. The parameter that describes this is given by

\[
\Gamma = \frac{Q^2}{4\pi\varepsilon_0 b k_b T_{p,k}},
\]

where \(Q\) is the charge on the particles, \(T_{p,k}\) is the kinetic temperature of the particles, and \(b\) is the interparticle distance. This distance is given by

\[
b = \sqrt[3]{\frac{3}{4\pi n_d}},
\]

where \(n_d\) is the dust particle density. In a plasma screening of charge is important and as a result the coupling parameter \(\Gamma\) changes to

\[
\Gamma = \frac{Q^2}{4\pi\varepsilon_0 b k_b T_{p,k}} \exp\left(-\frac{b}{\lambda_D}\right),
\]

where a Debye-Hückel potential is assumed. A plasma is strongly coupled when \(\Gamma \geq 1\), and Coulomb crystals can form if the coupling parameter is larger than a critical value:

\[
\Gamma \geq \Gamma_c = 170.
\]

Furthermore it is necessary that the interparticle distance \(b\) is smaller than the Debye length \(\lambda_D\).
3. The interaction between light and dust

Particles trapped in a plasma can be visualized with various light sources. The particles scatter the incident light and especially for monochromatic light the scattering profile is a signature of the size and the optical properties of the particle. From the profile some of the particle parameters can be extracted with the use of the Mie theory [45 - 48]. In this chapter this theory will be described. Furthermore, attention will be paid to Stokes vectors and Mueller matrices. With the use of this vector algebra the transport and interaction of polarized light with matter can be described.

3.1 Mie theory

The Mie theory describes the scattering of a plane wave by a homogeneous and isotropic sphere. In Fig. 3.1 the problem is depicted in spherical coordinates; a \( x \)-polarized wave impinges on a sphere and is scattered. A scattering matrix \( \tilde{S} \) that transforms the incident light into the scattered light can describe this scattering [46]. This is represented by

\[
\begin{pmatrix}
E_s \\
E_i 
\end{pmatrix} = \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} e^{-ikr + ikz} \begin{pmatrix} E_p \\ E_i \end{pmatrix}
\]

(3.1)

where \( E_{s,p} \) and \( E_{ip,is} \) are the scattered and incident components of the electric field respectively, \( r \) the radial distance and \( k \) the wave number in vacuum. The matrix \( \tilde{S} \) consists of the components \( S_1 \ldots S_4 \)

![Figure 3.1](image)

**Figure 3.1:** A beam of \( x \)-polarized light is scattered by a spherical particle. The propagation directions of the incident and the scattered wave define the scattering plane. The angles \( \varphi \) and \( \theta \) are defined with respect to this plane.
This electromagnetic problem needs to be described in spherical coordinates \((r, \theta, \phi)\). It is necessary that the well-known Maxwell equations, which are given by

\[
\begin{align*}
\nabla \cdot \vec{E} &= 0, \\
\nabla \cdot \vec{H} &= 0, \\
\nabla \times \vec{E} &= -\mu \frac{\partial \vec{H}}{\partial t}, \\
\nabla \times \vec{H} &= \varepsilon \frac{\partial \vec{E}}{\partial t},
\end{align*}
\]

are satisfied, where \(\varepsilon\) and \(\mu\) are the electric permittivity and the magnetic permeability of the medium. The Maxwell equations can be simplified by assuming an \(\exp(-i\omega t)\) time dependence, where \(\omega\) is the circular frequency of light, and by using the vector identity:

\[
\nabla \times \nabla \times \vec{A} = -\Delta \vec{A} + \nabla (\nabla \cdot \vec{A}).
\]

This results in the Helmholtz equations

\[
\begin{align*}
\Delta \vec{E} + k^2 \vec{E} &= 0, \\
\Delta \vec{H} + k^2 \vec{H} &= 0,
\end{align*}
\]

where \(\vec{E}\) and \(\vec{H}\) are complex vector functions representing the complex space part of the waves [49], and \(k\) is the wave number defined as

\[
k = \omega \sqrt{\varepsilon \mu}.
\]

Elementary solutions to the scalar wave equation

\[
\Delta \phi + k^2 \phi = 0,
\]

are well-known and are given by

\[
\phi_{nl} = \frac{\cos l \phi}{\sin l \phi} \left( P_n^l (\cos \theta) z_n(kr) \right).
\]

Here \(n\) and \(l\) are integers with \(n \geq l \geq 0\); the first factor is either a sine or a cosine. The second factor is an associated Legendre polynomial of degree \(n\) and order \(m\). The last factor \(z_n(kr)\) may be any spherical Bessel function. The spherical Bessel functions are connected to the ordinary Bessel functions via:

\[
z_n(kr) = \sqrt{\frac{\pi}{2k}} Z_{n+1/2}(\rho).
\]
Elementary solutions to the vector wave equations (3.4) can be found by means of the vector functions $M$ and $N$ that are defined by

$$\begin{align*}
M &= \nabla \times (r\phi), \\
N &= \frac{\nabla \times M}{k},
\end{align*}$$

(3.9)

where $r$ is the radius vector and $\phi$ is a function that obeys the scalar wave equation. Both functions $M$ and $N$ are divergence free, and moreover the vector functions $M$ and $N$ are also related via

$$\nabla \times N = kM.$$ 

(3.10)

Therefore $M$ and $N$ have all the properties of an electromagnetic field and it is possible to expand a plane wave into the spherical harmonics $M_{o,eln}$ and $N_{o,eln}$ (see [45, 50]). The result for the incident plane wave is given by

$$\begin{equation}
\vec{E}_{\text{incident}} = E_0 \sum_{n=0}^{\infty} i^n \frac{2n+1}{n(n+1)} (\vec{M}^{(i)}_{eln} - i\vec{N}^{(i)}_{eln}),
\end{equation}$$

(3.11)

where the superscript $(1)$ indicates the use of $j_n(kr)$ and the subscript $o$ and $e$ indicate odd and even. In a comparable manner the magnetic field can be expanded.

Now it is possible to solve the Mie scattering problem. Assume that a plane wave, polarized in the $x$-direction is incident on an isotropic, homogeneous sphere. Then it is necessary to fulfill the boundary conditions at the surface of the sphere:

$$\begin{align*}
(\vec{E}_i + \vec{E}_s - \vec{E}_{\text{int}}) \times \vec{e}_r &= 0, \\
(\vec{H}_i + \vec{H}_s - \vec{H}_{\text{int}}) \times \vec{e}_r &= 0,
\end{align*}$$

(3.12)

where the subscripts $i$, $s$, and $\text{int}$ correspond to the incident, scattered and internal field respectively. The internal field can be written as an expansion of spherical harmonics:

$$\vec{E}_{\text{int}} = E_0 \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (c_n \vec{M}^{(i)}_{eln} - id_n \vec{N}^{(i)}_{eln}),$$

(3.13)

where $c_n$ and $d_n$ are coefficients for the internal field. The same holds for the scattered field

$$\vec{E}_s = E_0 \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (-b_n \vec{M}^{(3)}_{eln} + ia_n \vec{N}^{(3)}_{eln}),$$

(3.14)

where the superscript $(3)$ indicates the use of the spherical Hankel function $h_n^{(1)}(kr)$ for an outgoing spherical wave; $r$ represents the radial distance, and $a_n$ and $b_n$ are the scattering coefficients. The spherical Hankel function shows asymptotic behavior at large distances from the sphere; this is approximately equal to:
\[ h_n^{(1)}(kr) = \frac{(-i)^n e^{i kr}}{i kr}. \] (3.15)

It is convenient to introduce the Riccati-Bessel functions

\[ \psi_n(\rho) = \rho j_n(\rho), \]
\[ \zeta_n(\rho) = \rho h_n^{(1)}(\rho), \] (3.16)

in order to simplify the expressions for the expansion coefficients. For further simplification, the dimensionless variable \( \rho = kr \) is introduced. The expansion coefficients can be found with help of the boundary conditions assuming that the magnetic permeability is equal inside and outside the sphere. This results in four linear equations in the expansion coefficients:

\[
\begin{align*}
\psi_n(x) - a_n \zeta_n(x) - mc_n \psi_n(y) &= 0, \\
\psi_n(x) - a_n \zeta_n'(x) - c_n \psi_n'(y) &= 0, \\
\psi_n(x) - b_n \zeta_n(x) - d_n \psi_n(y) &= 0, \\
\psi_n(x) - b_n \zeta_n'(x) - md_n \psi_n'(y) &= 0,
\end{align*}
\] (3.17)

where the size parameters \( x \) and \( y \) are introduced together with the relative refractive index \( m \). The boundary conditions only rule the radial changes at the boundary of the sphere. Therefore, these expressions contain only the radial dependency of the solutions and their radial derivatives. The size parameters are defined as

\[
x = \frac{2\pi r}{\lambda},
\]
\[
y = mx.
\] (3.18)

The set of equations can be solved for the expansion coefficients:

\[
\begin{align*}
a_n &= \frac{\psi_n'(y)\psi_n(x) - m\psi_n(y)\psi_n'(x)}{\psi_n(y)\zeta_n(x) - m\psi_n(y)\zeta_n(x)}, \\
b_n &= \frac{m\psi_n'(y)\psi_n(x) - \psi_n(y)\psi_n'(x)}{m\psi_n(y)\zeta_n(x) - \psi_n(y)\zeta_n(x)}, \\
c_n &= \frac{\psi_n(x)\zeta_n'(x) - \psi_n'(x)\zeta_n(x)}{m\psi_n(y)\zeta_n(x) - \psi_n(y)\zeta_n(x)}, \\
d_n &= \frac{\psi_n(x)\zeta_n'(x) - \psi_n'(x)\zeta_n(x)}{\psi_n(y)\zeta_n'(x) - m\psi_n(y)\zeta_n(x)}.
\end{align*}
\] (3.19)

Now the electric field in the far-field can be written as [49]
The interaction between light and dust

\[ E_\theta = -iE_0 \cos \varphi \frac{e^{ikr}}{kr} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos \theta) + b_n \tau_n(\cos \theta)], \]

\[ E_\varphi = iE_0 \sin \varphi \frac{e^{ikr}}{kr} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos \theta) + b_n \tau_n(\cos \theta)], \]

\[ E_r = 0, \]

with

\[ \pi_n(\cos \theta) = \frac{P'_n(\cos \theta)}{\sin \theta}, \] (3.21)

\[ \tau_n(\cos \theta) = \frac{d}{d\theta} \frac{P'_n(\cos \theta)}. \] (3.22)

Now, the resulting amplitude functions [46] can simply be read by comparing Eq. 3.1 with Eq. 3.20:

\[ S_1 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos \theta) + b_n \tau_n(\cos \theta)], \]

\[ S_2 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos \theta) + b_n \tau_n(\cos \theta)], \]

\[ S_3 = S_4 = 0. \]

Note that \( S_2 \) is connected to \( E_\theta \) and therefore lies in the scattering plane. Furthermore \( S_1 \) is related to \( E_\varphi \) and is perpendicular to the scattering plane. In the far-field the scattered intensity is measured; in the point \((r, \theta, \varphi)\) this intensity amounts up to

\[ I = [i_1(\theta) \sin^2 \varphi + i_2(\theta) \cos^2 \varphi] \frac{I_0}{(kr)^3}, \]

where \( I_0 \) the irradiance of the incident light and \( i_1(\theta) \) and \( i_2(\theta) \), see Fig. 3.2, are the far-field scattered intensities, for the perpendicular and parallel polarization respectively, and are given by:

\[ i_1(\theta) = |S_1|^2, \]

\[ i_2(\theta) = |S_2|^2. \] (3.24)
3.2 Stokes vectors and Mueller matrices

Stokes vectors

Light, like all types of vector waves, has the property of polarization. Polarization refers to the behavior with time of one of the field vectors appropriate to that wave observed at a fixed point in space [51]. When light is considered, the electric field vector determines the polarization. Unfortunately, the electric field vector is not a convenient observable for practical purposes because it is far too short (approximately $10^{-15}$ s) to be detected [52]. However, the polarization of a beam of monochromatic or quasi-monochromatic light can be described by irradiances. To that purpose G.G. Stokes introduced four quantities that are functions only of observables of the electromagnetic wave, now known as the Stokes parameters [53]. Together the four Stokes parameters constitute a Stokes vector $\vec{I}_{\text{qov}}$ that is defined by

$$\vec{I}_{\text{qov}} = \begin{pmatrix} I \\ Q \\ U \\ V \end{pmatrix} = \begin{pmatrix} I_0 \\ I_s - I_y \\ I_{\pi/2} - I_{-\pi/2} \\ I_r - I_l \end{pmatrix} = \begin{pmatrix} E_p^*E_p + E_sE_s^* \\ E_p^*E_p - E_sE_s^* \\ E_p^*E_s^* + E_sE_p^* \\ i(E_p^*E_s - E_s^*E_p) \end{pmatrix}$$

(3.25)
where $I$, $Q$, $U$, and $V$ are the four Stokes parameters, $E$ indicates the electric field and the subscripts $p$ and $s$ are the parallel and perpendicular (senkrecht) components; the superscript * indicates the complex conjugate. The Stokes parameters are irradiances as indicated by the symbol $I$, where $I_0$ is the total irradiance of the beam, and $Q$, $U$, and $V$ specify the state of polarization. The other used subscripts refer to a certain direction: $x$ and $y$ denote horizontal and vertical directions, $+\pi/4$ and $-\pi/4$ are $+45^\circ$ and $-45^\circ$ azimuths, and $r$ and $l$ denote right and left circular directions. The positive rotation direction is counterclockwise when looking into the source [51, 54]. The Stokes parameters can be measured with the help of linear and circular polarizers, e.g. $Q$ can be determined by placing a linear polarizer into a beam of light after measuring $I_0$. The polarizer is then turned into the $x$ and $y$-direction where $I_x$ and $I_y$ are measured. Now $Q$ is known. In a comparable manner $U$ and $V$ can be determined; $U$ is measured with a linear polarizer, and $V$ with a circular polarizer. In Eq. 3.26, two examples of Stokes vectors are given:

\[
\begin{pmatrix}
1 \\
 \cos 2\phi \\
 \sin 2\phi \\
0
\end{pmatrix}.
\]

Here the first vector represents horizontally polarized light, and the second one represents light polarized at an angle $\phi$ with respect to the plane of incidence; both vectors are totally polarized. Stokes vectors can also be used to represent partially polarized or unpolarized light [5]. Interaction of Stokes vectors with matter (e.g. optical components) is described with Mueller matrices.

**Mueller matrices**

Mueller matrices are 4*4 matrices that describe the interaction of light, represented by a Stokes vector with optical components. Multiplication of a Mueller matrix $\mathbf{M}_{\text{matter}}$ with a Stokes vector $\mathbf{I}_{\text{quv,in}}$ results in a new Stokes vector $\mathbf{I}_{\text{quv,out}}$:

\[
\mathbf{I}_{\text{quv,out}} = \mathbf{M}_{\text{matter}} \mathbf{I}_{\text{quv,in}}.
\]

The Mueller matrix formulation is based on the Stokes vectors and as a consequence the Mueller matrices can also be used to represent the propagation of partially polarized quasi-monochromatic light. Thus Mueller matrices can be used to express depolarizing optical systems, this in contrast with other methods like the Jones matrix method [51].

A perfect linear polarizer with a horizontal transmission axis can be represented by

\[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}.
\]

Unfortunately polarizers are not always perfect and they only show partial attenuation of the light wave. When the attenuation coefficient is $\alpha$, the partial linear polarizer is defined by:
The \( x \)-\( y \) reference frame can be rotated to another direction. The corresponding Mueller matrix for the rotation is given by

\[
\begin{bmatrix}
1 + \alpha & 1 - \alpha & 0 & 0 \\
1 - \alpha & 1 + \alpha & 0 & 0 \\
0 & 0 & 2\sqrt{\alpha} & 0 \\
0 & 0 & 0 & 2\sqrt{\alpha}
\end{bmatrix}^{\frac{1}{2}} \tag{3.29}
\]

where the rotation angle is indicated with \( \theta \). With the simple operation

\[
\vec{R}_{rot}(-P) \tilde{M}_{pol} \vec{R}_{rot}(P), \tag{3.31}
\]

it is possible to calculate the properties of a linear polarizer that is rotated over an angle \( P \) with respect to the \( x \)-axis; \( \vec{R}_{rot} \) and \( \tilde{M}_{pol} \) represent the rotation and polarization Mueller matrix respectively.

Reflection at a surface can be represented by

\[
\begin{bmatrix}
1 & -\cos 2\Psi & 0 & 0 \\
-\cos 2\Psi & 1 & 0 & 0 \\
0 & 0 & \sin 2\Psi \cos \Delta & \sin 2\Psi \sin \Delta \\
0 & 0 & -\sin 2\Psi \sin \Delta & \sin 2\Psi \cos \Delta
\end{bmatrix} \tag{3.32}
\]

where \( \Psi \) and \( \Delta \) are the well-known ellipsometric quantities. They obey the relation

\[
\rho = \frac{r_p}{r_s} \equiv \tan \Psi \exp(i\Delta), \tag{3.33}
\]

where \( r_p \) and \( r_s \) represent the reflection coefficients:

\[
r_p = \frac{E_{rp}}{E_{ip}}, \quad r_s = \frac{E_{rs}}{E_{is}}. \tag{3.34}
\]

Here \( E_{ip}, E_{is}, E_{rp}, \) and \( E_{rs} \) denote amplitudes of an electromagnetic wave, where the subscripts \( i \) and \( r \) correspond to the incident and the reflected wave, and the subscripts \( p \) and \( s \) correspond to the parallel and perpendicular (senkrecht) direction with respect to the plane of incidence respectively. Besides reflection on planar surfaces, light can interact
with spherical particles according to the Mie theory. The Mueller matrix for a single, spherical, homogeneous particle is:

\[
\frac{1}{2k^2r^2} \begin{bmatrix}
|S_1|^2 + |S_2|^2 & |S_2|^2 - |S_1|^2 & 0 & 0 \\
|S_2|^2 - |S_1|^2 & |S_1|^2 + |S_2|^2 & 0 & 0 \\
0 & 0 & 2\Re(S_1S_2^*) & -2\Im(S_1S_2^*) \\
0 & 0 & 2\Im(S_1S_2^*) & 2\Re(S_1S_2^*)
\end{bmatrix},
\]

(3.35)

where \(S_1\) and \(S_2\) are the amplitude functions from the Mie theory, \(k\) is the propagation number (in vacuum), and \(r\) is the radial distance.

A component that is often used is a retarder; often it is referred to as compensator. A retarder is a device that introduces a relative phase shift \(\Delta_c\) between the two eigenpolarizations of light. In principle the relative amplitude of the eigenpolarizations is not affected, but in practice it is affected; this is denoted by \(\tan\Psi_c\). The resulting Mueller matrix for a non-ideal retarder is:

\[
\begin{bmatrix}
1 & \cos 2\Psi_c & 0 & 0 \\
\cos 2\Psi_c & 1 & 0 & 0 \\
0 & 0 & \sin 2\Psi_c \cos \Delta_c & \sin 2\Psi_c \sin \Delta_c \\
0 & 0 & -\sin 2\Psi_c \sin \Delta_c & \sin 2\Psi_c \cos \Delta_c
\end{bmatrix}
\]

(3.36)
4. Dust particles monitored with a rotating compensator ellipsometer

4.1 Introduction

Laser light scattering has often been applied to determine the presence of and to visualize dust particles in radio-frequency plasmas. Some authors [23, 26, 27, 31 - 33] use the scattering only to visualize the particles in the discharge, while others analyze the scattered light at a static angle [55] or as a function of angle [56]. Furthermore, static techniques have been used to measure the ratio of horizontal to vertical polarization [14, 57 – 62] and subsequently to determine particle size. Continuously measuring the polarization has also been applied by using ellipsometric techniques [24, 25, 63, 64]. This diagnostic uses a rotating analyzer to modulate the polarization state of the laser light. The modulation increases the sensitivity of the detection system and the accuracy of the determination of the particle size improves. In this chapter, ellipsometric data will be presented which have been obtained with a rotating compensator ellipsometer. This ellipsometer has several advantages with respect to the rotating analyzer [53, 65, 66], which is the main reason for its application in the analysis of the oxidation process of polymer particles trapped in an RF oxygen plasma.

The advantages of a rotating compensator ellipsometer (RCE) above a rotating analyzer ellipsometer (RAE) are:

1. The non-ambiguous determination of \( \Delta \). In RAE only the cosine of \( \Delta \) is determined and thus it is impossible to distinguish between \( \Delta \) and \( 360^\circ - \Delta \). RCE can make this distinction.

2. The insensitivity of RCE to source and detector polarization; the compensator is placed between two fixed polarizers that cancel out a possible partial polarization of the source or the polarization sensitivity of the detector.

3. The possibility to determine the ellipsometric angles \( \Psi \) and \( \Delta \) without the necessity to use the DC level. RCE determines 5 Fourier coefficients of which only 3 are needed.

4. A complete determination of the Stokes vector.

This chapter starts with a short introduction to rotating compensator ellipsometry followed by a description of the used setup. The chapter ends with a discussion of the results and conclusions. The contents of this chapter have been published in [67].

4.2 RCE theory

In Fig. 4.1 the used configuration is shown for the ellipsometer. In this configuration the emitted laser light interacts with a polarizer, the sample under investigation, a rotating compensator (quarter wave plate), and an analyzer before the light impinges upon the detector.
Figure 4.1: The used configuration for the ellipsometer. The light from the light source (argon ion laser) is vertically polarized, interacts with an object under investigation e.g. a collection of spheres and is analyzed by a detection system consisting of a compensator, an analyzer and a detector.

Mathematically this setup can be represented by a series of matrix multiplications:

\[
\vec{I}_{\text{out}} = \tilde{R}(-A) \cdot \vec{M}_A \cdot \tilde{R}(A-C) \cdot \vec{M}_{\Psi,\Delta} \cdot \tilde{R}(C) \cdot \vec{M}_{\Psi,\Delta} \cdot \tilde{R}(-P) \cdot \vec{M}_P \cdot \tilde{R}(P) \cdot \vec{I}_{\text{in}},
\]

where the incident Stokes vector \( \vec{I}_{\text{in}} \) is changed and the detector measures the intensity of the transmitted Stokes vector \( \vec{I}_{\text{out}} \); \( \vec{M}_{\Psi,\Delta} \) and \( \vec{M}_{\Psi,\Delta} \) are Mueller matrices describing the behavior of the retarder and the sample under investigation respectively. \( P, C, \) and \( A \) are the azimuth angles of the various components. Due to the rotating compensator the detected intensity \( I(C) \) has \( 2C \) and \( 4C \) contributions, where \( C \) is the periodically changing azimuth angle of the compensator:

\[
I(C) = (A_0 + A_1 \cos 2C + B_1 \sin 2C + A_4 \cos 4C + B_4 \sin 4C) I_p, \tag{4.2}
\]

and with the help of a Fourier analysis the Fourier coefficients \( A_0, A_2, B_2, A_4, \) and \( B_4 \) can be determined. In the continuation of this chapter the laser intensity \( I_p \) is equal to 1. Via Eq. 4.1 these coefficients are linked to the properties of the sample under investigation

\[
\begin{align*}
A_0 &= 1 - \frac{1}{4}(1 + y_c) \cos 2\Psi, \\
A_2 &= x_c (1 - \cos 2\Psi), \\
B_2 &= x_c \sin 2\Psi \cos \Delta + z_c \sin 2\Psi \sin \Delta, \\
A_4 &= -\frac{1}{4}(1 - y_c) \cos 2\Psi, \\
B_4 &= \frac{1}{4}(1 - y_c) \sin 2\Psi \cos \Delta,
\end{align*}
\tag{4.3}
\]

where for convenience’s sake it is already assumed that the azimuth angles of polarizer (45°) and analyzer (0°) are known. The terms \( x_c, y_c, \) and \( z_c \) represent the non-ideal behavior of the rotating compensator.
Dust particles monitored with a rotating compensator ellipsometer

\[ x_c \equiv \cos 2\Psi_c = 0, \]
\[ y_c \equiv \sin 2\Psi_c \cos \Delta_c \approx 0, \]  \hspace{1cm} (4.4)
\[ z_c \equiv \sin 2\Psi_c \sin \Delta_c \approx 1, \]

and a characterization procedure is necessary to obtain the magnitude of these terms; this has been described in detail by Den Boer [53]. In order to obtain the ellipsometric angles \( \Psi \) and \( \Delta \) from the Fourier coefficients it is important to note that:

1. The \( A_2 \) Fourier coefficient depends on \( x_c \) and thus is close to zero. Therefore this Fourier coefficient will introduce large errors and will not be used.
2. \( A_0 \) is the DC component of the intensity and may contain interference of external light sources, e.g., plasma emission. Its use should be avoided.
3. In ellipsometry the use of absolute intensities is avoided. As a consequence the ratio of Fourier coefficients needs to be used instead of absolute values.

Finally three Fourier coefficients remain and \( A_4 \) is used to scale the two others. Taking the compensator characteristics into account two intermediate quantities \( X_1 \) and \( X_2 \) can be defined as

\[ X_1 \equiv \tan 2\Psi \sin \Delta = \frac{x_c B_4}{z_c A_4} - \frac{1 - y_c}{2z_c} \frac{B_2}{A_4}, \]
\[ X_2 \equiv \tan 2\Psi \cos \Delta = -\frac{B_4}{A_4}, \]  \hspace{1cm} (4.5)

and subsequently the ellipsometric angles can be written as

\[ \tan 2\Psi = \sqrt{X_1^2 + X_2^2}, \]
\[ \tan \Delta = \frac{X_1}{X_2}. \]  \hspace{1cm} (4.6)

Sign information of the Fourier coefficients helps to find the exact values for \( \Psi \) and \( \Delta \), where \( 0^\circ \leq \Psi < 90^\circ \) and \( 0^\circ \leq \Delta < 360^\circ \).

When a spherical particle is investigated, the Fourier coefficients depend on the scattering amplitude functions \( S_1 \) and \( S_2 \), because the Mueller matrix now contains only the elements \( S_1 \) and \( S_2 \) of the scattering matrix. The Fourier coefficients are given by:

\[ A_0 = \frac{(1 - y_c) |S_1|^2 + (3 + y_c) |S_2|^2}{4k^2 r^2}, \]
\[ A_2 = \frac{x_c |S_2|^2}{k^2 r^2}, \]
\[ B_2 = \frac{x_c \Re(S_1 S_2^*) - z_c \Im(S_1 S_2^*)}{k^2 r^2}, \]  \hspace{1cm} (4.7)
\[ A_4 = \frac{(1 - y_c) |S_2|^2 - |S_1|^2}{4k^2 r^2}, \]
\[ B_4 = \frac{(1 - y_c) \Re(S_1 S_2^*)}{2k^2 r^2}. \]
and analysis of the Fourier coefficients yields the ellipsometric angles $\Psi$ and $\Delta$. Note that the choice for evaluating $\Psi$ and $\Delta$ lies in the fact that these quantities unlike the Fourier coefficients are independent on the choice of the experimental setup.

### 4.3 Experimental Setup

The ellipsometry measurements have been performed in an aluminum test reactor consisting of two tubes (cylindrical diameter: 150 mm, height: 180 mm) with easy optical access. The reactor has been described in detail elsewhere [34, 68 - 70] and is depicted in Fig. 4.2. At the bottom of the tubes an RF-electrode is installed (diameter: 120 mm). The RF-electrode has been modified in order to provide easy optical accessibility of the injected powders.

![Diagram of the reactor](image)

**Figure 4.2:** A schematic picture of the reactor. The reactor consists of two aluminum tubes stacked on top of each other; the dashed line indicates the boundary between the two tubes. The RF electrode has been modified in order to provide easy optical access; therefore, a saucer is put on top of the RF electrode. This saucer also enhances the trapping of the particles.

An aluminum cylinder was placed on the RF-electrode and on top of this a saucer was placed to enhance particle trapping in the plasma and to increase the optical access.

The light source is a Lexel 85-7 argon-ion laser that emits vertically polarized light and is operated at 488 nm with an output power of 300 mW. The laser light becomes linearly polarized with an azimuth of 45° after interaction with a Glan-laser prism polarizer (Melles Griot 03PGL301/A). The detection system consists of a rotating compensator (quarter wave plate) with an anti-reflection coating (Melles Griot 03WRQ04/488/078), a sheet polarizer (Melles Griot 03FPG007) and a photomultiplier (Thorn EMI QL 30F/RFI). The compensator is mounted in a motor-driven encoder (Heidenhain ERN620 encoder) that rotates at a frequency of $\omega = 37.5$ Hz.
Dust particles monitored with a rotating compensator ellipsometer

Figure 4.3: A SEM photograph of the melamine formaldehyde particles. The particles on the photo have a size of 12.2 µm and a refractive index $n=1.68 \pm 0.05$. The SEM photograph is taken by C. Eggs, Department of Physics, University of Greifswald.

In Fig. 4.3 an illustrative SEM photograph of the melamine formaldehyde (MF) particles [MicroParticles GmbH, Berlin] is shown; the SEM photograph is taken by C. Eggs, Department of Physics, University of Greifswald. The particles in the picture have an average size of 12.2 µm and a refractive index $n=1.68 \pm 0.05$. These particles have been chosen for a number of reasons:

1. The particles are highly monodisperse and have proven to be functional for the injection in plasmas, e.g. Thomas [23] used these particles for the creation of Coulomb crystals.
2. The particles supposedly do not react in argon plasmas, and thus have a constant size and refractive index, which is known. This can be used to calibrate several optical diagnostics.
3. The particles are made of polymer material and therefore can be etched in e.g. oxygen plasmas.
4. The polymer material is highly cross-linked, and thus the particle will not fall to pieces, due to electron bombardment, or hostile and reactive environments.

For the measurements in this chapter, MF particles with an average size of 4.79 µm ± 0.08 µm have been used. Note that there are some irregularities: some particles are smaller and some particles stick together like ‘twins.’

4.4 Results

In Fig. 4.4 a typical Mie scattering RCE measurement is shown.
Figure 4.4: A typical etching measurement of MF particles trapped in an oxygen RF plasma. For clarity only one out of ten measurement points is shown. The RF plasma is operated at 130 Pa, 20 sccm, and 36 W. According to the supplier, the used MF particles have a diameter $2r_p = 4.79 \pm 0.08 \mu m$.

The MF particles are injected in a RF oxygen plasma which is operated at 36 W, 130 Pa, and 20 sccm. 58 s after injection of the particles the measurement started; this time was needed to open the slit protecting the photomultiplier and to adjust the operating voltage of the photomultiplier. In the plasma the particles acquire a negative charge, which results in their suspension in the sheath. There the particles are arranged in a solid-like structure, which did not change much during the first forty minutes of the measurement. This has been observed visually. The different layers of the solid were clearly visible, due to the light scattering by the individual particles. Also the vertical stacking of the layers, reported by other authors [30, 32] could be observed. The layers seem to be stable and this is due to the creation of a wake and an ion-focusing region. The increased ion density in the ion-focusing region provides for an attractive force that restores the stability of the different layers. The particles could only be observed from the side, therefore no estimation of the number of particles in the scattering volume could be made.

In the plasma the particles are oxidized and the changes in their scattering properties are monitored. The ellipsometric angles at the beginning of the measurement are $\Psi = 65^\circ$ and $\Delta = -25^\circ$, where $\Delta$ is made negative to obtain a smooth curve (normally $\Delta$ ranges from $0^\circ$ to $360^\circ$); the accuracy is approximately $2^\circ$ in both the ellipsometric angles. The measurement curve is an asymmetric helix, which converges clockwise to $\Psi = 57^\circ$ and $\Delta = 0^\circ$. The intensity changes, which are periodic in $2C$ and $4C$, are detected by the photomultiplier while the compensator rotates and an I/O board records the signal. After one full rotation of the compensator the signal is analyzed; this takes 2 s. This measurement time is limited by the computer speed and memory. Despite the speed limitations, only 10 % of the measurement data is shown in Fig. 4.4; the time interval between the consecutive points is approximately 24 s. The measurement has been stopped...
at \( t = 2600 \) s after it has been observed visually that the particles started to leak out of the plasma, or were blown away by the oxygen flow.

In order to find the relation between the ellipsometric angles and the particle size it is necessary to perform simulations [71 - 73] based on Mie theory [45 - 48]. In the simulations the particles are assumed to remain homogeneous, spherical, and mono-disperse in size. Furthermore it is assumed that the particle modification in the plasma does not alter their refractive index. Based on the Mie theory, \( S_1(\theta, \varphi) \) and \( S_2(\theta, \varphi) \) can be calculated for various radii, complex refractive indices, wavelengths, scattering angles and azimuth angles of the light. For a refractive index \( m = 1.68 \), wavelength \( \lambda = 488 \) nm, scattering angle \( \theta = 90^\circ \) and azimuth angle \( \varphi = 45^\circ \) the particle size \( 2r_p \) was varied from 4.70 to 4.90 \( \mu \)m in steps of 0.1 Å. Using equation (2.33) the amplitude functions \( S_1(\theta, \varphi) \) and \( S_2(\theta, \varphi) \) are linked to the ellipsometric angles; this is shown in Fig. 4.5. The strange spikes present in the plot are caused by resonances in the Mie scattering coefficients \( a_n \) and \( b_m \), see Eq. (3.19) and [45, 74 - 76]. These calculations directly show the necessity to use size distribution functions to relate calculated ellipsometric angles to measured ones because of the large number of particles present in the scattering volume in the experimental situation.

![Figure 4.5](image-url)

**Figure 4.5:** The ellipsometric angles calculated for a growing, non-absorbing particle according to Mie theory. The ellipsometric angles are plotted from -90° to 270° instead of the regular values 0° to 360° in order to get a smoother plot. The particle diameter was varied from 4.70 to 4.90 \( \mu \)m for a refractive index \( m = 1.68 \), \( \lambda = 488 \) nm, scattering angle \( \theta = 90^\circ \), and an azimuth angle \( \varphi = 45^\circ \).

Therefore a first attempt is made by assuming a normal distribution of the particles with a constant standard deviation of 0.05 \( \mu \)m (with respect to the distribution at the beginning of the simulation) and a decreasing mean size during the etching process; this simulation is shown in Fig. 4.6.
Figure 4.6: Simulation of the ellipsometric angles taking the size dispersion of the particles into account. A gaussian distribution is assumed with a constant standard deviation of 0.05 µm and a decreasing mean size. The simulation starts at $\Psi = 67^\circ$ and $\Delta = -20^\circ$ and ends at $\Psi = 55^\circ$ and $\Delta = -30^\circ$.

The beginning at $\Psi = 67^\circ$ and $\Delta = -20^\circ$ is in a good agreement with the experimental situation, however a larger particle size $2r_p = 4.88$ µm has to be assumed. According to the supplier the particles have a diameter $2r_p = 4.79 \pm 0.08$ µm.

The simulation does not show the same behavior as the measurement; the typical helix-like structure is missing. This leads to the conclusion that not only the size but also the size dispersion should be varied. This has been done in several simulations where a linearly increasing standard deviation with etching time (and thus with decreasing particle size) has been assumed. This leads to better results. Some of the simulations show the helix-like structure e.g. the simulation shown in Fig. 4.7, where the standard deviation is allowed to increase from 0.05 µm to 0.11 µm.

Hayashi [63] applied a translation operated log-normal size distribution to simulate the growing of carbon soot in a methane plasma. A log-normal distribution is a distribution of a random variable whose logarithm is distributed normally [77]. In Fig. 4.8 an example of a log-normal distribution is given. If log-normal data are subjected to a log transformation a normal distribution results with the well-known mean $\mu$ and standard deviation $\sigma$. In a normal distribution 68% of the distribution can be found in the range $[\mu - \sigma, \mu + \sigma]$, whereas for a log-normal distribution 68% can be found in the range $[\mu^*/\sigma^*, \mu^*+\sigma^*]$ where $\mu^*$ and $\sigma^*$ are the transformed mean and standard deviation.
**Figure 4.7:** The helix-like structure that resulted from a translation operated normal distribution where the size dispersion increased from 0.05 µm (mean size = 4.68 µm) to 0.11 µm (mean size = 4.08 µm).

**Figure 4.8:** An example of a log-normal size distribution (solid line) which exhibits the typical skew shape. The distribution is also plotted on a logarithmic scale (dashed line) and then it constitutes a normal distribution.

This distribution has been applied to the etching process of particles because it was expected that the etching process might influence the symmetry of the distribution; then a
log-normal distribution is a more flexible tool. The result of the simulation with a log normal distribution is shown in Fig. 4.9.

Figure 4.9: Simulation of the measurement assuming a translation operated log-normal size distribution. The geometric standard deviation increased from $\sigma = 1.02$ at the start to $\sigma = 1.06$ at the end of the measurement. The average diameter of the particle is $2r_p = 4.88 \ \mu m$ at the start and $2r_p = 4.32 \ \mu m$ at the end. The simulation shows the typical helix-like structure but misses the asymmetric form.

In the simulation an initial particle size of $2r_p = 4.88 \ \mu m$ has been taken in order to find ellipsometric angles comparable to the measurement. The geometric standard deviation is found to be $\sigma = 1.02$ at the beginning of the measurement and it increases linearly to $\sigma = 1.06$ at the end. The change in the particle size is $\delta(2r_p) = 0.56 \ \mu m$. The normal and the log-normal simulations more or less yield the same result: they both lack the asymmetric behavior, the standard deviations need to be increased, and the change in particle diameter is approximately $0.6 \ \mu m$. However, the log-normal simulation is slightly more resembling to the measurement shown in Fig. 4.4.

The necessity to increase the standard deviations for both size distribution functions can indicate that the oxidation rate is not the same for all the suspended particles. An explanation for this apparent non-uniform oxidation can be the relative position of the particles in the sheath. The particles are trapped in several layers, and each layer is situated above another. Particles that are comparable in size and situated in different layers are subjected to bombardment by ions and electrons. The ions are accelerated towards the electrode and thus gain energy. Dust particles that are hit by more energetic ions are etched faster. Therefore it can be expected that the particles situated in layers closer to the RF electrodes are etched faster than particles situated in higher layers. This will lead to an increase of the size dispersion.

To explain the observed behavior of the phase shift $\Delta$, it is necessary to study the scattered Stokes vector. It consists of irradiances that result from the components of the
Dust particles monitored with a rotating compensator ellipsometer

Van de Hulst [46] represents the scattered components of the electric field by:

\[ E_p = a_p e^{-i\epsilon_1} e^{-iz+ia}, \]
\[ E_s = a_s e^{-i\epsilon_2} e^{-iz+ia}, \]

(4.8)

where \( a_p \) and \( a_s \) are positive amplitudes and \( \epsilon_1, \epsilon_2 \) are phases, and \( \Delta = \epsilon_1 - \epsilon_2 \). This gives a scattered Stokes vector represented by:

\[
\begin{bmatrix}
I \\
Q \\
U \\
V
\end{bmatrix} = \frac{1}{a_p^2 + a_s^2} \begin{bmatrix}
a_p^2 + a_s^2 \\
a_p^2 - a_s^2 \\
2a_p a_s \cos \Delta \\
2a_p a_s \sin \Delta
\end{bmatrix}.
\]

(4.9)

Now we observe in Fig 4.5 that with increasing size dispersion, \( \Delta \) can attain almost all possible values between 0° and 360°. As a result, the phases \( \epsilon_1 \) and \( \epsilon_2 \) and the resulting phase shift \( \Delta \) possibly behave as stochastic variables. The expectation value of \( \Delta \) then becomes \( <\Delta> = 0 \), which is observed.

For the other ellipsometric angle, \( \Psi \), the final value is \( \Psi = 57^\circ \). Substituting this value in Eq. 3.35 and subsequent comparison with Eqs. 3.32 and 4.9, indicates that the scattered Stokes vector has a preference for light polarized parallel with the plane of incidence: \( Q/I = 0.4 \), and \( a_p/a_s = 1.54 \). Unfortunately, no approximations or rules of thumb are available for scattering under 90° for particles of this size. For very small particles, the observed scattering will be Rayleigh scattering which is uniform for light polarized perpendicular to the plane and has a \( \cos \theta \) dependence, with \( \theta \) the scattering angle, for the light polarized parallel with the plane. Furthermore, the Rayleigh scattered intensity \( I \) depends on wavelength \( \lambda \) and particle size \( r_p \): \( I \propto r_p^6 / \lambda^4 \). For very large spheres the scattering can be approximated by Fraunhofer diffraction.

If we assume that scattering on the particles with an increasing size dispersion leads to a stochastic behavior of the two positive amplitudes \( a_p \) and \( a_s \), then the \( Q \) component will have an expectation value of \( <Q> = 0 \), and this is not equal to the observation. In Fig. 3.2 the behavior of the scattered intensities \( i_1(\theta) \) and \( i_2(\theta) \) is shown for one particle radius. Note that \( i_2(\theta) \), which is connected to perpendicular polarized light, shows sharper details than \( i_1(\theta) \) and this is true for a large range of radii. Therefore, more \( i_1(\theta) \) than \( i_2(\theta) \) will be measured for scattering under 90°, especially when the solid angle is taken into account. As a result, \( a_p/a_s \) should be expected to be dominated by the parallel-polarized light. This is in accordance with our observation.

Besides the increase of the size dispersion and arguments based on the Stokes vector, other explanations can be provided for the measured behavior. The surface of the particle can be changed due to chemical reactions. Chemical reactions on the surface can result in layers with different refractive indices. Assuming a different refractive index for a single layer particle has a large impact on the simulation results. \( \Psi \) and \( \Delta \) change dramatically in value; \( \Psi \) shifts to values below 45° and the value of \( \Delta \) is no longer around 0° and 360° but is close to 180°. Simulations like Fig. 4.10 clearly show helix-like structures, but the curve ends at wrong values for \( \Psi \) and \( \Delta \).
Figure 4.10: A plot of the ellipsometric angles when a particle is grown with a complex refractive index $m = 1.68 - 0.1i$. The particle size $r_p$ was varied from 0.6 to 2 $\mu$m. The curve starts at $\Psi = 36^\circ$ and $\Delta = 120^\circ$ (0.6 $\mu$m) and ends at $\Psi = 20^\circ$ and $\Delta = 177^\circ$ (2.0 $\mu$m).

Figure 4.11: The ellipsometric behavior for a coated particle. The coating of the particle is assumed to be constant with a complex refractive index $m_{\text{shell}} = 1.68 - 0.1i$ and a thickness of $r_{\text{shell}} = 10$ nm. The core size was varied from $2r_{\text{core}} = 4.7$ to 4.9 $\mu$m while the refractive index of the core was kept constant at $m_{\text{core}} = 1.68$. The simulation starts at $\Psi = 47^\circ$ and $\Delta = 65^\circ$ and ends at $\Psi = 47^\circ$ and $\Delta = 249^\circ$. 
It is also possible that the particle acquires a coating layer or that a reaction layer is present. In this case the description of the scattering properties need to be modified. Several authors [45, 47, 78] derived formulae for coated particles and in Fig. 4.11 a simulation of the resulting ellipsometric behavior is shown. In the simulation the particle had a core size that was varied from $2r_{\text{core}} = 4.7$ to $4.9 \mu\text{m}$ and $m_{\text{core}} = 1.68$, while the shell had a constant thickness of $r_{\text{shell}} = 10 \text{ nm}$ and a complex refractive index $m_{\text{shell}} = 1.68 - 0.1i$. Coated particles did not lead to correct values for $\Delta$. Therefore no further attempts to fit the measured data are performed. The assumption that the particle is coated increases the number of variables and complexity of the fitting procedure; this can easily lead to mistakes.

Another effect, which can influence the experimental $\Psi$-$\Delta$ curve, might be the nonuniformity of the oxidation process over the particle surface. This could change the particle shape during oxidation. However, we assume that the particles are spinning and that the oxidation is sufficiently uniform to preserve their original spherical shape. In Fig. 4.12 both the measurement and the simulation (log-normal distribution) are shown.

![Diagram](image)

**Figure 4.12:** Experimental (dashed line) and simulation curve (solid line) for the oxidation of MF particles.

The two curves intersect at some points; the simulation has been optimized for intersection points. Plotting the simulation size against experimental time obtained at the intersection points results in the time dependence of the particle size; this is displayed in Fig. 4.13. It can be seen that the particle radius decreases linearly with time. The slope of this line, which indicates the etch rate, is not sensitive to experimental errors in the ellipsometric parameters.
Figure 4.13: The particle radius is shown as a function of measurement time. The resulting etch rate is $1.1 \text{ Ås}^{-1}$.

An etch rate of $1.1 \text{ Ås}^{-1}$ has been determined. In comparison with the etching of surfaces the etch rate for the particles is low. Investigations on the etching of polymer surfaces in oxygen discharges have been performed in the same reactor by Swinkels [79]. He investigated the etching behavior of polystyrene (PS, $m_{ps} = 1.59$) and polymethylmethacrylate (PMMA, $m_{pmma} = 1.488$) layers on a silicon wafer with a photo-elastic modulator ellipsometer. In order to accurately monitor the etching of these polymers, the oxygen plasma was operated at low RF power (13 W, 10 Pa, 11 sccm O$_2$); etch rates of 8 and 4 Ås$^{-1}$ have been found for PMMA and PS respectively. The fact that the etch rate for the particles is low compared to the etch rate for polymers on a surface can be understood, as in ion-assisted etching the energy of incident ions is an important parameter. The particles, suspended in the plasma, remain at the floating potential, which is in the order of several volts. This is much lower than the plasma sheath voltage (several hundreds of volts), so the energy of positive ions at the particle surface is substantially lower than at the electrode surface and consequently lower etch rates for particles can be expected.

4.5 Conclusions

In this chapter Mie scattering rotating compensator ellipsometry has been applied to monitor the etching of melamine formaldehyde particles trapped in a radio-frequency oxygen plasma. The measurements have been fitted with the simulation data, based on the Mie scattering theory, in order to determine the time dependent particle size. The experimental behavior of the ellipsometric parameters can be explained if a change in the size distribution of the particles during the oxidation process is taken into account. The measurement is best fitted assuming a translation operated log-normal size distribution with increasing size dispersion. The size of the particles decreases linearly with etching time and an etch rate of $1.1 \text{ Ås}^{-1}$ has been determined.
5. Mueller Matrix Ellipsometry

5.1 Introduction

In the previous chapter it was pointed out that the dust particles probably remained spherical during the oxidation process in the plasma. However, in principle a possible change of the particle shape can be verified; the Mie theory provides us with several tools to check this assumption for various circumstances [45, 46].

Spherical particles preserve the polarization direction, i.e. perpendicularly polarized light remains perpendicular. Non-spherical particles do not preserve polarization: they exhibit cross polarization. Cross polarization is manifested in the $M_{22}$ element of the Mueller matrix; this element no longer equals $M_{11}$.

One can also check the full Mueller matrix. For a spherical particle the Mueller matrix has the simple form indicated in Eq. 3.35. In case of spheroids (non-spherical bodies of revolution [80]) the matrix changes where the cross polarization remains the observable quantity. When the particles become even more irregular, all the matrix elements become nonzero elements. Regarding this the construction of a Mueller matrix ellipsometer (MME), capable of measuring the full Mueller matrix has been started [81 - 85]. The difference with the ellipsometer of chapter 4 is that now a setup with two rotating compensators, one at the source side and one at the detector side is realized. In this chapter the theory connected to MME will be explained. Furthermore attention will be paid to the calibration procedure of all MME components. This chapter will be finished with a discussion of the results obtained with the MME. The measurements have been performed in a Gaseous Electronics Conference (GEC) RF Reference cell, and we will start with an introduction of this cell from a historical perspective.

5.2 Historical perspective of the GEC cell

In radio frequency plasmas the discharge characteristics can be strongly affected by the configuration of the electrodes and chamber, materials of construction, design of the power circuitry, and location of the diagnostic probes [86, 87]. Also several reactor conditions like surface conditioning and feed gas impurities can play a role. This causes reliability problems: plasma processes run on the same reactor may fail mysteriously from time to time, and processes run under comparable circumstances on several different reactors can yield divergent results. It is obvious that differences in experimental data generated due to differences in reactor conditions cannot be separated from the effects of different reactor geometries. As a result less meaningful comparisons can be made between data obtained on different reactors, and it becomes more difficult to validate models.

At the 1988 Gaseous Electronics Conference a workshop was held in order to address the problems of data comparison and model validation. Here, several researchers agreed that the development of a reference cell could help to facilitate comparisons of experimental and theoretical data. Furthermore, the discharge geometry and a ‘minimum diagnostic tool set’ for the reference cell had to be specified. The diagnostic chosen was the measurement of voltage and current waveforms in a high-purity argon discharge. The measurements can be used to determine whether seemingly identical reference cells operated similar. Further demands were that the cell could be easily replicated and have a
simple design, compatible with a variety of diagnostics, compatible with a variety of reactive gases, and related to industrial geometries. Finally, the reactor was unofficially named the ‘GEC RF Reference cell.’

5.3 Experimental setup

Fig. 5.1 shows a schematic cross section of the GEC RF Reference cell vacuum chamber.

Figure 5.1: A schematic cross section of the GEC RF Reference Cell. 1: cooling water inlet, 2: gas inlet, 3: RF power connection (bottom) and ground connection (top), 4: moveable upper electrode assembly, 5: showerhead electrode, 6: ground shield, 7: tee to turbo molecular pump, 8: symmetric pumping manifold.

The main chamber, ports, and manifold are made of electropolished stainless steel. The flanges on the top and on the bottom of the reactor are 33.66 cm in diameter, and the inner diameter of the chamber is 25.1 cm. The height of the vacuum chamber is 22.2 cm. The chamber is equipped with 8 ports in three different sizes, 7 cm, 15.25 cm, and 20.3 cm. The largest ports provide optical access beyond the discharge region, while the four small ports provide access solely to the discharge region. They can be used for several diagnostics like pressure gauges, Langmuir probes but also for the injection of dust.
Figure 5.2: A photograph of the GEC RF reference cell. In the cell an argon discharge is struck. Both electrodes are visible; the upper electrode is moveable and is now positioned 6.35 cm above the bottom electrode. The upper electrode is a showerhead electrode that is used for gas injection; it has 169 equally spaced holes of 0.3 mm diameter placed on concentric circles. The feeding gas is pumped out via the symmetric pumping manifold, which partly can be seen, in the right corner of the photograph. The picture is taken by M. M. Hemerik.

A photograph of the GEC cell that is being used in Eindhoven is shown in Fig. 5.2. On top of the reactor we have mounted the moveable upper electrode. The electrode distance can be varied from 1.27 to 6.35 cm. The upper electrode has a showerhead electrode that has 169 equally spaced holes (0.3 mm diameter) placed on concentric circles. This water-cooled electrode is used to supply the gas (argon and oxygen in our case) to the discharge region. The electrode is isolated from the chamber by a Teflon insulator. Ground shields surround the insulator. The ground shields reduce the sputtering of the Teflon and furthermore they ensure that the electrical field is more uniform in the area between the electrodes.

The gas is pumped out via the pumping manifold. This manifold was designed to improve the gas flow characteristic at pressures above 13.3 Pa and it restricts the chamber pumping speed when attempting to operate at low pressures. We apply two pumps on the reactor in order to maintain operating and UHV conditions namely a turbo molecular pump, Edwards EXT250 (He: 250 l/s) and a high vacuum pump, Edwards E2M40 (11.8 l/s). The turbo molecular pump is connected to one of the 15.25 cm ports via a bellows and a tee. A Programmable Logic Controller (PLC, Siemens Simatic TD200) unit controls the pumps and the unit further controls the water and gas supply. Three PLC-controlled valves determine the pumping path. One of the valves is a MKS 253B throttling valve (butterfly valve) that is used to maintain the operating pressure inside the reactor. The two other valves are Norcal 11212-0150R and 11212-0400R valves that are used to switch from operating regime to UHV regime. The pressure inside the reactor is monitored using three pressure gauges, one of that is a Balzers TPR 250 compact Pirani gauge which is used to monitor the pressure near the high vacuum pump. A Balzers PKR 250 compact full range gauge is used to monitor the whole pumping down procedure (down to UHV
conditions). The operating regime is monitored with a MKS 127 AAX baratron that has a 1 mbar range (100 Pa). Standard operating pressure is 20 Pa, at a flow rate of 3 sccm. The flow rate is controlled by a Bronkhorst Hi-tec F-200C-FA mass flow controller. The RF power is set between 2 and 40 W. The plasma is created at a frequency of 13.56 MHz using a Hewlett-Packard 33120A frequency generator, a Kalmus 150C wideband RF-amplifier and a home built T-type matching network. The generated power is measured using a Bird model 4410A power meter.

During plasma operation we are able to inject dust into the discharge region. Therefore a manipulator arm is mounted to one of the 4 small ports of the reactor. A small cylinder with a sieve as bottom is mounted on the manipulator arm and contains the dust particles.

The entire reactor is moveable in the vertical direction. Additional information on the setup will be given in the chapters that treat the experimental work.

5.4 Theoretical background on the Mueller Matrix Ellipsometer

In the previous chapter a simplified mathematical representation of a rotating compensator ellipsometer was presented. Here a more general representation of an ellipsometer is given

\[ \vec{I}_{\text{out}} = \vec{A} \vec{M}_{\Psi\Delta} \vec{P} \cdot \vec{I}_{\text{in}}, \]  

(5.1)

where the light beam represented by the incident Stokes vector interacts with a Polarization State Generator (PSG) \( \vec{P} \) [88], then interacts with the optical system \( \vec{M}_{\Psi\Delta} \) under investigation, and is finally detected by a Polarization State Detector (PSD) \( \vec{A} \). The transmitted Stokes vector is incident on a detector where the first component of this vector (intensity) is analyzed. The object under investigation is represented by a 4\(^{\times}\)4 matrix given in Eq. (5.2):

\[
\vec{M}_{\Psi\Delta} = \begin{bmatrix}
M_{11} & M_{12} & M_{13} & M_{14} \\
M_{21} & M_{22} & M_{23} & M_{24} \\
M_{31} & M_{32} & M_{33} & M_{34} \\
M_{41} & M_{42} & M_{43} & M_{44}
\end{bmatrix}.
\]  

(5.2)

This matrix has 16 elements and 9 independent relations between the elements exist, so 7 independent constants can be measured [51]. The PSG and PSD can consist of different optical components; here polarizers and compensators are chosen, because this combination provides a complete measurement of the Stokes vector. A mathematical representation is given in Eqs. (5.3) and (5.4) for PSG and PSD respectively:

\[ \vec{P} = \hat{R}(-C) \cdot \vec{M}_{\Psi\Delta} \cdot \hat{R}(C - P) \cdot \vec{M}_P \cdot \hat{R}(P), \]  

(5.3)

and

\[ \vec{A} = \hat{R}(-A) \cdot \vec{M}_A \cdot \hat{R}(A - C_d) \cdot \vec{M}_{\Psi\Delta d} \cdot \hat{R}(C_d). \]  

(5.4)
In these equations $\vec{R}$ represents the necessary rotations and $\vec{M}$ are matrices describing the behavior of the polarizer and compensators; a subscript $d$ indicates the detector side. Exchanging the source and detector and reversing the direction of propagation interchanges the functions of PSG and PSD, i.e. the setup is symmetric [88]. PSG and PSD are both complete and thus capable of measuring the entire Stokes vector from the analysis of a single signal. As a consequence of the completeness of PSG and PSD the ellipsometer is also complete, i.e. it is capable of measuring the full Mueller matrix.

In contrast with [84, 85] the light source emits vertically polarized light and this alters the Stokes vector generated by the PSG:

\[
\begin{bmatrix}
I \\
Q \\
U \\
V
\end{bmatrix} = (1 - \cos(2P))
\begin{bmatrix}
1 + x_v \cos(2P - 2C) \\
f \cos(2P - 4C) + x_v \cos(2C) + (1 - f) \cos(2P) \\
-f \sin(2P - 4C) + x_v \sin(2C) + (1 - f) \sin(2P) \\
-z_v \sin(2P - 2C)
\end{bmatrix} I_p ,
\]

where $f = \frac{1}{2} - \frac{1}{2}y_c$ and $I_p$ is the laser irradiance. This Stokes vector interacts with the optical system under investigation and the emerging Stokes vector $[I_d \ Q_d \ U_d \ V_d]^T$ (T indicates transpose) is subsequently analysed by the PSD. The measured intensity $I_{det}$ is given by

\[
2I_{det} = I_d [x_{cd} \cos(2C_d - 2A) + 1] + \\
Q_d [f_d \cos(4C_d - 2A) + x_{cd} \cos(2C_d) + (1 - f_d) \cos(2A)] + \\
U_d [f_d \sin(4C_d - 2A) + x_{cd} \sin(2C_d) + (1 - f_d) \sin(2A)] + \\
V_d [-z_{cd} \sin(2C_d - 2A)],
\]

where the subscript $d$ indicates the detector side. The detector response $I_{det}$ can be written down as a Fourier series in $C_d$:

\[
I_{det}(C_d) = A_0 + A_2 \cos 2C_d + A_4 \cos 4C_d + B_2 \sin 2C_d + B_4 \sin 4C_d ,
\]

and with an azimuth setting of the analyzer at $A = 90^\circ$ the Fourier coefficients are given by

\[
A_0 = (g/2)[I_d - (1 - f_d)Q_d],
\]

\[
A_2 = (g/2)[-x_{cd}I_d + x_{cd}Q_d],
\]

\[
B_2 = (g/2)[x_{cd}U_d + z_{cd}V_d],
\]

\[
A_4 = (g/2)[-f_dQ_d],
\]

\[
B_4 = (g/2)[-f_dU_d],
\]

with $g$ the gain of the detector. Here we assume that the gain is independent of frequency. These five coefficients contain all the polarimetric information available from the measurement. Note that $A_2$ again depends on $x_c$ and thus is close to zero. This equation can be solved for the output Stokes parameters.
thereby providing a complete determination of polarization state from the Fourier analysis of a single waveform.

To determine the full Mueller matrix of the optical system under investigation the azimuth angles of polarizer and analyzer are fixed at $P = 90^\circ$ (polarization state of the laser is fully transmitted) and $A = 90^\circ$. The variation of the input Stokes vector on the sample varies with $C$ according to

\[
\begin{bmatrix}
I \\
Q \\
U \\
V
\end{bmatrix} =
\begin{bmatrix}
1 & -x_c & 0 & 0 & 0 \\
-1+f & x_c & 0 & -f & 0 \\
0 & 0 & x_c & 0 & -f \\
0 & 0 & -z_c & 0 & 0
\end{bmatrix}
\begin{bmatrix}
1 \\
\cos 2C \\
\sin 2C \\
\cos 4C \\
\sin 4C
\end{bmatrix} I_p,
\]

(5.10)

where some of the matrix elements have negative signs compared with the article of Hauge [85] due to the polarizer azimuth. The transformation from input to output Stokes vector is described by

\[
\begin{bmatrix}
I_d \\
Q_d \\
U_d \\
V_d
\end{bmatrix} =
\begin{bmatrix}
M_{11} & M_{12} & M_{13} & M_{14} \\
M_{21} & M_{22} & M_{23} & M_{24} \\
M_{31} & M_{32} & M_{33} & M_{34} \\
M_{41} & M_{42} & M_{43} & M_{44}
\end{bmatrix}
\begin{bmatrix}
1 & -x_c & 0 & 0 & 0 \\
-1+f & x_c & 0 & -f & 0 \\
0 & 0 & x_c & 0 & -f \\
0 & 0 & -z_c & 0 & 0
\end{bmatrix}
\begin{bmatrix}
1 \\
\cos 2C \\
\sin 2C \\
\cos 4C \\
\sin 4C
\end{bmatrix} I_p
\]

(5.11)

Thus, each of the output Stokes parameters $I_{quv,k}$ ($k = 1...4$, and indicates the component of the Stokes vector) can be expressed as a Fourier series in the azimuth angle $C$ (at the generating side):

\[
I_{quv,k} = (E_{k0} + E_{k2} \cos 2C + F_{k2} \sin 2C + E_{k4} \cos 4C + F_{k4} \sin 4C) I_p.
\]

(5.13)

The output Stokes parameters $I_{quv,k}$ are subjected to Fourier analysis with respect to azimuth angle $C$. Therefore it is necessary to use a number of $l$ ($l > 4$) different settings of the compensator azimuth $C_q$, beginning at $0^\circ$ with equal increments over a $180^\circ$ range:
\[ C_q = (q - 1)180^\circ / l, \]  
\[ (q = 1 \ldots l). \]  
The Fourier analysis of the parameters \( I_{qu,v,kl} \) results in the determination of the matrix elements \( E_{kl} \) and \( F_{kl} \). If we call the matrices on the right hand side in equations 5.11 and 5.12 \( \vec{B} \) and \( \vec{E} \), respectively, we can simplify to
\[
\vec{E} = MB. \tag{5.15}
\]

The elements of \( \vec{E} \) are determined from the second Fourier analysis, while the elements of \( \vec{B} \) are determined from the calibration of \( C \). Equation 5.15 can be inverted and this results in
\[
\vec{M} = \vec{E}B^T(BB^T)^{-1} = \vec{E}\vec{F}, \tag{5.16}
\]
where \( T \) is the transpose and \( \vec{F} \) is a matrix that is completely determined by the defect parameters of the compensator \( C \). \( \vec{F} \) is given by
\[
\vec{F} = 
\begin{bmatrix}
(f + x_e^2) / h & x_e^2 / h & 0 & 0 \\
x_e(1 - 2f) / h & x_e / h & 0 & 0 \\
0 & 0 & 0 & -1 / z_c \\
(f - 1 - x_e^2) / h & -(1 + x_e^2) / h & 0 & 0 \\
0 & 0 & -1 / f & -x_e / z_c f
\end{bmatrix}, \tag{5.17}
\]
\[
h = f(2x_e^2 + 1) \cong 0.5. \tag{5.18}
\]

With the help of this defect matrix \( \vec{F} \) the full Mueller matrix for the sample can be determined.

### 5.5 The calibration of the optical system

An extremely necessary step when working with ellipsometers is the calibration of all optical components [53]. All different azimuth angles have to be determined; for the polarizer and analyzer this is simply done with two parabolic fits, while varying the azimuth angles around the minimum. This minimum is found by minimizing the transmitted intensity until it reaches a minimum. To enhance the accuracy, the azimuth angles are varied around this minimum and with a parabolic fit the ‘real’ minimum is found. For the compensators the azimuth angles have to be determined, i.e. what is the position of the fast axis of the compensators with respect to the reference frame. Furthermore it is important to know the compensator imperfections. One expects that the compensator introduces a relative phase shift of 90° between the two eigenpolarization of light. Thereby the relative amplitude ratio of both eigenpolarizations is not affected in principle. However, in practice the exact retardation, or the relative phase shift will not be
90° but equal to \( \Delta_c \). The relative amplitude ratio will not remain 1, but will change; this value is denoted by \( \tan \Psi_c \). These are the compensator imperfections, and they are also indicated with the term defect parameters.

Azimuth angles and defect parameters play an important role in the analysis. The calibration is done in a straight-through measurement with one compensator present and

\[
\begin{align*}
\text{P} & \quad \text{C} & \quad \text{A} & \quad \text{Detector}
\end{align*}
\]

**Figure 5.3:** Schematic setup of a straight-through calibration. The polarizer \( P \) is turned to 45°, the analyzer \( A \) to 90°, and the automatic compensator \( C \) rotates. The detector records the transmitted intensity.

the polarizer and analyzer azimuth angles are \( P=45° \) and \( A=90° \), see Fig. 5.3. This compensator has an azimuth angle, suppose that this angle is \( C_1 \) with respect to the scattering plane (plane of incidence) and then the detector response for this variable compensator azimuth \( C \) is given by

\[
I_{\text{det}}(C - C_1) = A_0 + A_2 \cos(2(C - C_1)) + B_2 \sin(2(C - C_1)) + A_4 \cos(4(C - C_1)) + B_4 \sin(4(C - C_1)),
\]

and a Fourier analysis (indicated with subscript \( F \)) gives the following coefficients

\[
\begin{align*}
A_{0F} &= A_0, \\
A_{2F} &= A_2 \cos 2C_1 - B_2 \sin 2C_1, \\
B_{2F} &= B_2 \cos 2C_1 + A_2 \sin 2C_1, \\
A_{4F} &= A_4 \cos 4C_1 - B_4 \sin 4C_1, \\
B_{4F} &= B_4 \cos 4C_1 + A_4 \sin 4C_1.
\end{align*}
\]

These coefficients need to be corrected for the azimuth angle \( C_1 \) and the real Fourier coefficients (subscript \( R \)) can easily be found:

\[
\begin{align*}
A_{0R} &= A_{0F}, \\
A_{2R} &= A_{2F} \cos 2C_1 + B_{2F} \sin 2C_1, \\
B_{2R} &= B_{2F} \cos 2C_1 - A_{2F} \sin 2C_1, \\
A_{4R} &= A_{4F} \cos 4C_1 + B_{4F} \sin 4C_1, \\
B_{4R} &= B_{4F} \cos 4C_1 - A_{4F} \sin 4C_1.
\end{align*}
\]

Now the compensator on the generator side can be added for calibration. It is calibrated in a straight-through Mueller matrix measurement where the surface under investigation is air (characterized by the identity matrix) and its azimuth angle is known in advance. A schematic setup is shown in Fig. 5.4.
Figure 5.4: A schematic representation of the used setup for the straight-through Mueller matrix measurement that is performed to determine the calibration matrix of the stepper motor driven compensator $C$ on the source side. The automatic compensator on the detector side is indicated by $C_d$. The azimuth angles of polarizer and analyzer are fixed to 90°.

The result of the Mueller measurement is matrix $\tilde{E}$

$$
\tilde{E} = \begin{bmatrix}
1 & e_{02} & f_{02} & e_{04} & f_{04} \\
e_{10} & e_{12} & f_{12} & e_{14} & f_{14} \\
e_{20} & e_{22} & f_{22} & e_{24} & f_{24} \\
e_{30} & e_{32} & f_{32} & e_{34} & f_{34}
\end{bmatrix},
$$

(5.22)

with normalized coefficients $e_{ij} = E_{ij}/E_{00}$ and $f_{ij} = F_{ij}/E_{00}$ and thus the defect parameters are given by

$$
x_c = -e_{02} = e_{12} = f_{22},
$$

$$
f = -e_{14} = -f_{24} = e_{10} - 1,
$$

$$
z_c = -f_{32}.
$$

(5.23)

The fact that several matrix elements are equal to the defect parameters serves as a consistency check for the calibration.

### 5.6 Results

In this part the results obtained with Mueller matrix ellipsometry on single spherical particles and clouds of particles, approximately 12 µm in diameter, in oxygen and argon plasmas, will be described. Therefore the setup described in the previous chapter has been enhanced. An extra compensator (Melles Griot 16WFQ375) with an anti-reflection coating has been added. This compensator is mounted on a stepper motor which can rotate with a maximum speed of 20° s\(^{-1}\). Furthermore, the Lexel argon ion laser has been replaced by a 2W Coherent Innova 70 argon ion laser; the laser is operated at a wavelength of 488 nm, at a constant output power of 25 mW during all the measurements. The last change concerns the reactor: the RCE measurements have been performed in an aluminum test reactor, while the MME measurements are performed in the GEC RF reference cell.
5.6.1 Accuracy

In order to perform Mueller matrix ellipsometry it is necessary to perform a very accurate calibration of all the optical components that are used in this optical diagnostic. Goldstein et al. [34] have shown that small errors in the determination of the azimuth angles and/or of the compensator imperfections can very easily lead to errors up to 30% in each separate or all the matrix elements. Imposing an error upon e.g. the polarizer azimuth led to errors of 10% in some of the matrix elements for the used Mueller matrix ellipsometer.

Besides the correct determination of azimuth angles and the compensator imperfections, it is also necessary to determine the number of steps \( l \) as indicated in Eq. 5.14. Therefore, this number has been varied from 5, which is the minimum, up to 180. In Fig. 5.5 the behavior of the \( M_{22} \) element is shown as function of the number of steps. In a straight-through mode the object under investigation is air; air does not alter the properties of the polarized light and as a result the measured Mueller matrix should be the identity matrix.

![Graph showing the behavior of the M22 component as a function of the number of steps.](image)

**Figure 5.5:** The \( M_{22} \) component (squares) of the Mueller matrix in a straight-through measurement as a function of the number of compensator steps. The minimum number of steps necessary to perform a Fourier transformation is 5; this can lead to large deviations. Increasing the number of steps leads to a reduction of this standard deviation, and also to a better determination of the component, which must be equal to 1. The total measurement time (hollow circles) has also been depicted; it increases linear with the number of steps.

It is clear from Fig. 5.5 that with an increasing number of steps the value of \( M_{22} \) becomes more accurate; this is also reflected in the other matrix elements. The minimum number of steps obviously yields divergent results with a relative large error. Moreover, a single disturbance of the signal will lead to totally wrong results. Therefore the minimum number of steps will not be used in any measurement.
In Fig. 5.5 also the measurement time is indicated, which increases with an increasing number of steps. This is caused by the limited speed of the steppermotor. The steppermotor does not directly attain its maximum speed, but needs to accelerate. With a large number of steps, the steppermotor no longer accelerates and thus limits the measurement time. Furthermore, the time needed to measure all signals increases linearly with time. Like in every practical laboratory situation, stability is a major issue. To investigate samples with Mueller matrix ellipsometry with a steppermotor, which has to be positioned at 180 azimuth positions, theoretically gives good results. However, in our setup the total measurement time while scanning 180 azimuth positions amounts 10 minutes and this leads to a reduction of the quality. For the $M_{22}$ element this lead to an average value of 0.98±0.06. Therefore, the number of steps will be determined by the obtained calibration results, i.e. a comparison of measurement and theoretical predicted values, and the total measurement time. Evaluation of the measured Mueller matrices and taking the measurement time into account indicates that 15 azimuth positions should be taken. In Table 5.1 the average Mueller matrix is shown that is measured in the straight-through mode. The $M_{11}$ component has been used to normalize all other components and as such its standard deviation equals zero. The measured Mueller matrix is equal to the expected identity matrix.

Table 5.1: The full Mueller matrix measured in a straight-through measurement; all elements are averaged 20 times. The number of steps of the steppermotor driven compensator was 15; the laser power was 25 mW. The $M_{11}$ element is used to normalize all elements and therefore by definition its average is 1 and its standard deviation is zero. The straight-through measurement resulted in a successful measurement of the identity matrix.

<table>
<thead>
<tr>
<th></th>
<th>-2E-4 ± 4E-3</th>
<th>-8E-3 ± 5E-3</th>
<th>-3E-5 ± 2E-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1E-3 ± 2E-3</td>
<td>1.02 ± 7E-3</td>
<td>-1E-2 ± 1E-2</td>
<td>-3E-3 ± 3E-3</td>
</tr>
<tr>
<td>2E-5 ± 3E-3</td>
<td>1E-2 ± 1E-2</td>
<td>1.0 ± 1E-2</td>
<td>-2E-3 ± 4E-3</td>
</tr>
<tr>
<td>3E-5 ± 3E-3</td>
<td>1E-3 ± 3E-3</td>
<td>1E-2 ± 3E-3</td>
<td>1.01 ± 5E-3</td>
</tr>
</tbody>
</table>

Besides calibration and measurement in a straight-through mode it is also necessary to perform measurements in the ‘measurement’ setup, i.e. with a reflection on an object under investigation. In order to perform reliable measurements in the reflection mode it is extremely important to determine the polarizer and analyzer azimuth again. The reflection on the object under investigation changes the reference frame, and as a result the polarizer, and especially the analyzer azimuth can change [51, 53]. Therefore an ordinary right-angle prism has been taken as the object under investigation, see Fig. 5.6.

The prism was incorporated into the setup and was positioned manually. The prism changed the propagation direction of the beam of light with 90°. The beam of light was bend in the horizontal plane. In Table 5.2 the results of the measurements on the prism are shown.
Chapter 5

Figure 5.6: The setup in the reflection mode. The angle $\phi_0$ is the angle of incidence and it will be used in Eq. 5.24.

Table 5.2: The full Mueller matrix measured in a reflection mode; the reflecting surface was an ordinary right-angle prism, and the angle of incidence was 45º. All elements of the matrix are averaged 20 times. The number of steps of the stepper motor driven compensator was 15; the laser power was 25 mW. The measurement resulted in a successful measurement of the properties of the prism. The prism does not attenuate one of the eigenpolarizations ($M_{21}=M_{12}=0$) and this gives a $\Psi = 44.5^\circ \pm 1^\circ$; the values of $M_{33}$, $M_{34}$, $M_{43}$, and $M_{44}$ indicate that the prism introduces a phase shift $\Delta = 30.6^\circ \pm 0.3^\circ$.

| $1$ | $-7E-3 \pm 3E-3$ | $9E-3 \pm 3E-3$ | $1E-2 \pm 2E-3$ |
| $3E-2 \pm 5E-3$ | $1.03 \pm 6E-2$ | $2E-2 \pm 5E-3$ | $-2E-1 \pm 4E-3$ |
| $-6E-3 \pm 2E-3$ | $1E-2 \pm 7E-3$ | $0.87 + 8E-3$ | $0.52 \pm 2E-3$ |
| $8E-3 \pm 1E-3$ | $6E-3 \pm 1E-2$ | $-0.52 \pm 3E-3$ | $0.89 \pm 5E-3$ |

From the $M_{21}$ and $M_{12}$ the $\Psi$ can be calculated; this results in $\Psi = 44.5^\circ \pm 1^\circ$. In a comparable manner the phase shift $\Delta$ can be calculated. To that purpose, the values of $M_{33}$, $M_{34}$, $M_{43}$, and $M_{44}$ can be used; see Eq. 3.32. These values indicate that the prism introduces a phase shift $\Delta = 30.6^\circ \pm 0.3^\circ$. With the help of an equation given by Azzam [51] this measurement can be analyzed:

$$\tan \frac{1}{2} \Delta = \frac{(n_1/n_0) \sqrt{[(n_0/n_1)^2 \sin^2 \phi_0 - 1]}}{\sin \phi_0 \tan \phi_0}, \quad (5.24)$$

where $\phi_0$ the angle of incidence, $n_1$ and $n_0$ the refractive index of the reflective medium (air) and the ambient (glass) respectively. This equation is only valid above the critical angle $\theta_c = \arcsin(n_1/n_0)$. It is assumed that the prism material is glass and the refractive index of glass is given by Palik [89] to be $n_0 = 1.463$; the critical angle is $\theta_c = 43.1^\circ$. Now it is possible to determine from Eq. 5.24 an angle of incidence $\phi_0 = 45.3^\circ \pm 0.1^\circ$; this is approximately equal to the expected angle of incidence of 45º.

If an angle of incidence of 45º is assumed then it is possible to determine the refractive index of the ambient material; Eq. 5.24 yields $n_0 = 1.47 \pm 10^{-3}$, which is close to the expected value. The critical angle associated with this refractive index is $\theta_c = 42.7^\circ$. 


5.6.2 Single particles in the discharge

Argon
Mueller matrix ellipsometry has been performed on a single MF particle trapped in an argon radio-frequency discharge. The single particle is trapped in the discharge in a modified potential created by a ring that is present on the electrode surface, see Fig. 1.2. Some of the matrix elements are shown in Fig. 5.7.

Figure 5.7: A single particle in a 20 Pa, 7.5 W argon discharge monitored with the Mueller Matrix ellipsometer; the laser power was 25 mW. Shown are the diagonal elements $M_{11}$ (solid line), $M_{22}$ (circles), $M_{33}$ (up triangle), and $M_{44}$ (down triangle). The matrix elements must obey the relations: $M_{11} = M_{22}$ and $M_{33} = M_{44}$. Obviously this is not the case for $M_{11}$ and $M_{22}$. The cause of these problems is unknown. Other particles were observed in the scattering volume after 70 minutes and therefore the measurement was stopped after 75 minutes. These particles probably were originally stuck to the top electrode and flaked off during plasma operation. The extra particles introduced in that way change the amount of the light scattered, and affect the stability of the particle trapping resulting in fluctuating signal values.

During the measurement, one single particle in a 20 Pa, 7.5 W argon discharge has been monitored with the Mueller Matrix ellipsometer. In Fig. 5.7 the diagonal elements $M_{11}$ (solid line), $M_{22}$ (circles), $M_{33}$ (up triangle), and $M_{44}$ (down triangle) are shown. The matrix elements must obey the relations: $M_{11} = M_{22}$ and $M_{33} = M_{44}$. Obviously this is not the case for $M_{11}$ and $M_{22}$. The cause of these problems is unknown, but it might be caused by uncertainties of the analyzer azimuth angle.

Furthermore, other particles were observed in the scattering volume and therefore the measurement was stopped after 75 minutes. These particles probably were stuck to the top electrode and flaked off during plasma operation. The particles can change the background emission, and surely change the amount of the light scattered. This might explain the observed problems.
A third problem concerns the determination of the ellipsometric angle $\Psi$; this angle can be determined with the use of $M_{12}$ or $M_{21}$. Analysis of the Mueller matrix indicates that a single particle depolarizes the light, which in principle is impossible if the particle is spherical and uniform. In the Mueller matrix (Eq. 3.32) the components have to obey the following relation:

$$M_{21}^2 + M_{33}^2 + M_{44}^2 = M_{12}^2 + M_{44}^2 + M_{44}^2 = 1,$$ (5.25)

and obviously this is not the case because $M_{33}$ and $M_{44}$ become larger than 1. This problem can have several causes that need to be checked in the future:
1. Errors in the position of the azimuth angles of the optical components.
2. Depolarization due to reactor windows.
3. Errors in the determination of the background signal of the plasma, or, even worse, fluctuations of the background signal.

As $\Psi$ is directly related to the value of the matrix elements $M_{12}$ or $M_{21}$, errors in the determination of these elements directly lead to large errors in $\Psi$. Luckily, the other ellipsometric angle, the phase shift $\Delta$, can be determined without the absolute value of the matrix elements. $\Delta$ can be determined from the ratio of matrix elements:

$$\Delta = \arctan \left( \frac{M_{44}}{M_{34}} \right) = \arctan \left( -\frac{M_{33}}{M_{43}} \right),$$ (5.26)

and this is of course less influenced by measurement errors. An ellipsometric plot showing both $\Psi$ and $\Delta$ is shown in Fig. 5.8. Note that the value of $\Psi$ is unreliable.

**Figure 5.8:** The behavior of the ellipsometric angles $\Psi$ and $\Delta$ in a 20Pa, 7.5W argon plasma; the laser power was 25 mW. Equation 5.25 does not hold for the measurement. As a consequence $\Psi$ is unreliable. The other ellipsometric angle, the phase shift $\Delta$, is determined using a ratio, see Eq. 5.26. Therefore that value is more realistic.
As the value of $\Delta$ is more reliable than the value of $\Psi$, one can attempt to find the particle properties size and refractive index by using the phase shift only. This complicates the fitting; a result is shown in Fig. 5.9, where it is assumed that the refractive index does not change during the measurement.

**Figure 5.9:** The behavior of the phase shift $\Delta$ as a function of measurement time; the measurement took 75 minutes. The measurement (squares) is performed in a 20 Pa, 7.5 W argon discharge; the laser power was 25 mW. A fit (solid line) is shown, indicating that the particle size changes during the measurement; a refractive index of 1.631 has been obtained. The size decreases with approximately 5 nm. This might be a measurement error caused by thermal variations, or unstable trapping of the particle. Furthermore, the particle might be etched due to contamination of the plasma by residual water (and hence oxygen). The measurement was stopped after 75 minutes, because other particles were observed in the scattering volume. These particles probably were stuck to the top electrode and flaked off during plasma operation.

In Fig. 5.9, the behavior of the phase shift $\Delta$ is shown as a function of the measurement time; the measurement took 75 minutes and was stopped because other particles appeared in the measurement volume. The appearance of other particles disturbs the stability and changes the scattering signal; as a consequence the measurement is stopped. The measurement (squares) is performed in a 20 Pa, 7.5W argon discharge. A theoretical curve (solid line) is compared with the measurement, suggesting that the particle size changes during the measurement; according to the simulation the particle has a refractive index equal to 1.631. From this simulation a size decreases results of approximately 5 nm. This
might be a measurement error caused by thermal variations, or unstable trapping of the particle. Furthermore, the particle might be etched due to contamination of the plasma by residual water in the reactor. The measurement was stopped after 75 minutes, because other particles were observed in the scattering volume. These particles probably were stuck to the top electrode and flaked off during plasma operation.

**Oxygen**
A single melamine formaldehyde particle has been trapped in an oxygen discharge for 3.5 hours without any problems, but then the signal became unstable. The plasma was operated at 20 Pa and 3 W. In Table 5.3 the results of the Mueller matrix measurement are shown for the non-diagonal elements. The measurement indicates that the particle remains spherical during the processing.

**Table 5.3:** The Mueller matrix belonging to a single particle floating in an oxygen discharge during 3.5 hour of processing. The plasma is operated at 20 Pa, and 3 W; the laser power was 25 mW. All non-diagonal elements remain zero during the processing indicating that the particle remains spherical.

<table>
<thead>
<tr>
<th></th>
<th>M_{21}</th>
<th>-1E-2 ± 2E-2</th>
<th>5E-3 ± 2E-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_{21}</td>
<td>1.05 ± 0.06</td>
<td>9E-3 ± 2E-2</td>
<td>9E-2 ± 2E-2</td>
</tr>
<tr>
<td>-7E-3 ± 3E-2</td>
<td>7E-3 ± 3E-2</td>
<td>M_{33}</td>
<td>M_{34}</td>
</tr>
<tr>
<td>-1E-2 ± 2E-2</td>
<td>-2E-2 ± 2E-2</td>
<td>M_{43}</td>
<td>M_{44}</td>
</tr>
</tbody>
</table>

In Fig. 5.10 the behavior of the $M_{41}$ component is shown as a function of the measurement time. The value of the element approximately remains zero indicating that the particle remains spherical during the oxygen processing.

**Figure 5.10:** The behavior of the $M_{41}$ component as a function of the measurement time. The total measurement in the oxygen discharge (20 Pa, 3 W) took about 3.5 hours; the laser power was 25 mW.
In Fig. 5.11 the behavior of $M_{21}$, $M_{34}$, and $M_{44}$ is shown; the values change and this indicates that the particle changes in size. Using these elements, an ellipsometric plot can be calculated, see Fig. 5.12. Like in the case of an argon discharge, the value of $\Psi$ is not reliable, so the plot should not be trusted. Again Eq. 5.25 does not hold during the measurement. Therefore the analysis is based only upon the value of the phase shift $\Delta$.

The result of the analysis of the measured data is shown in Fig. 5.13. The particle size at the start is 6.46 $\mu$m and the refractive index is 1.64; during the measurement the particle size gradually decreases to 6.41 $\mu$m. An etch rate of $3.7 \times 10^{-2}$ Ås$^{-1}$ has been determined. Compared to the change of the particle size in the argon plasma, $8.9 \times 10^{-3}$ Ås$^{-1}$, the value is significantly larger. As the laser output power in both experiments is kept at the same value, 25 mW, the change of the particle size in the oxygen plasma must be inflicted by the oxygen chemistry. Oxygen is a reactive gas and as a consequence it can be used to etch the particle material. However, there is a large difference between the etching of substrates placed on the electrode and the etching of a particle immersed in a plasma. The sheath in front of the powered electrode has a potential in the order of a few hundreds of Volts and this potential accelerates the positive ions to the surface. There the ions sputter and etch the substrate. The situation for the particle is different; the potential difference between the plasma and the particle is much smaller and is in the order of 1 – 10 V. As a consequence, the particle etching will be caused by low-energy ions and radicals. This can result in low etch rates.
Comparing the etch rate in this MME experiment with the etching of a cloud of dust particles (RCE measurement, chapter 4), then a large difference in the etching speed is found. The rotating compensator ellipsometer (RCE) measurements yielded an etch rate of 1.1 Ås\(^{-1}\), whereas the MME measurements yielded 3.7·10\(^{-2}\) Ås\(^{-1}\). However, there are some differences between the RCE measurements and the MME measurements, see Table 5.4.

Table 5.4: The main differences between the Rotating Compensator Ellipsometry measurements and the Mueller Matrix Ellipsometry measurements.

<table>
<thead>
<tr>
<th></th>
<th>RCE</th>
<th>MME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor</td>
<td>Aluminum test reactor</td>
<td>GEC cell</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>130 Pa</td>
<td>20 Pa</td>
</tr>
<tr>
<td>RF Power</td>
<td>36 W</td>
<td>3 W</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td>20 sccm</td>
<td>3 sccm</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>4.8 µm</td>
<td>12 µm</td>
</tr>
</tbody>
</table>
Figure 5.13: The phase shift $\Delta$ (circles) as a function of the measurement time (bottom axis). The fit is the solid line, and is plotted as a function of the particle radius (top axis); the obtained refractive index is 1.66. During the measurement that took 3.5 hours, the particle size changed with 50 nm. The etch rate is $3.7 \times 10^{-2}$ Ås$^{-1}$. This is a realistic value if the low RF power (3 W) is taken into account. During the measurement the laser output power was kept constant at 25 mW.

The differences in reactor design, RF power, flow rate, and pressure can lead to different plasma chemistries that complicate comparison of the etch rates. Different conditions (lower pressure, lower power) had to be taken in order to guarantee a stable trapping of the particles in the GEC cell with respect to the aluminum test reactor. Moreover, due to the different conditions the etch rate becomes lower, and therefore the observed changes take place at a lower rate.

5.6.3 Dust clouds in the discharge

Injecting a single particle into the plasma is a time-consuming task, however injecting a cloud of dust particles is easier. Here we show a MME measurement on a dust cloud in an argon discharge operated at 20 Pa and 8W, see Fig. 5.14 and Table 5.5.
Figure 5.14: The behavior of the $M_{12}$ (squares), $M_{21}$ (circles), $M_{34}$ (up triangle), and $M_{43}$ (down triangle) components of the Mueller matrix. The measurement was performed in a 20 Pa, 8W argon discharge on a cloud of particles. The number of compensator steps was 15 and the signal is averaged over ten periods. The laser power amounted 25 mW. Measuring one point in the graph takes 60 seconds; returning the steppermotor driven compensator into its starting position for a following measurement, analysis, data-storage, and graphical output takes 30s.

Table 5.5: $M_{11}$, $M_{22}$ and the non-diagonal elements of the Mueller Matrix measured on a cloud of dust particles trapped in a 20 Pa, 8W argon discharge. The values are averaged over 125 successive measurements (15 positions of the compensator) and the accompanying standard deviation. This clearly indicates that the particles remain spherical. Note the irregular value of $M_{22}$.

<table>
<thead>
<tr>
<th></th>
<th>$M_{12}$</th>
<th>$M_{21}$</th>
<th>$M_{34}$</th>
<th>$M_{43}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.3E-4 ± 0.01</td>
<td>0.04 ± 0.02</td>
<td>-1.5E-3 ± 8E-3</td>
<td></td>
</tr>
<tr>
<td>$M_{21}$</td>
<td>0.83 ± 0.02</td>
<td>0.04 ± 0.02</td>
<td>0.04 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>-0.01 ± 0.02</td>
<td>-0.02 ± 0.02</td>
<td></td>
<td>$M_{33}$</td>
<td>$M_{34}$</td>
</tr>
<tr>
<td>-8E-3 ± 7E-3</td>
<td>-0.03 ± 0.01</td>
<td>$M_{43}$</td>
<td>$M_{44}$</td>
<td></td>
</tr>
</tbody>
</table>

It can be observed from Table 5.5 that the particles remain spherical during the trapping in the argon discharge. Like in the case of a single particle, the particle size changes. This is shown in Fig. 5.15, where $\Delta$ is plotted against measurement time and particle radius. The other ellipsometric angle, $\Psi$, is not shown. Again, Eq. 5.25 did not hold for the matrix elements. However, in the case of a cloud of spherical particles depolarization can occur. This has been shown by Deirmendjian [90]. In spite of this fact, it is still possible that Eq. 5.25 does not hold due to other causes e.g. calibration of the Mueller matrix ellipsometer.
Figure 5.15: The phase shift $\Delta$ plotted as a function of the measurement time (bottom axis) and the average particle radius (top axis). The measurement, performed in a 20 Pa, 8 W argon plasma, takes 3 hours. The laser output power amounted 25 mW. A size change of 12 nm is observed, i.e. 0.01 Ås$^{-1}$; this is comparable to the measurement performed on a single particle in an argon discharge. Note that the average size is approximately 1 μm smaller than the measurements on single particles.

From Fig. 5.15 an ‘etch’ rate can be determined; this etch rate is equal to 0.01 Ås$^{-1}$ which is equal to the change in particle size for a single particle in a 20 Pa, 7.5 W argon discharge. The average refractive index of the particles is 1.64. The average size of the particles in Fig. 5.14 is smaller than in all the previous measurements. The main cause for this is the discharge; particles that are injected into the discharge obtain a charge and thus are trapped. Larger particles obtain a higher charge, but also have a higher radius and thus a larger mass. In equilibrium, the electrical force equals the gravitational force. The electric field in a discharge increases from the glow to the electrode. Therefore larger particles can be found closer to the electrode than smaller particles. In our experimental situation, the smaller particles showed more stable trapping, and ellipsometry was performed on these particles. As a result the average size of the particles is smaller than the size of the particles in all previous experiments.

In Fig. 5.15 a measurement of the scattered Stokes vector is shown; the solid line indicates the intensity $I$, a dashed line indicates $Q$, a dotted line represents $U$, and a dashed-dotted line depicts $V$. This vector obeys the theoretical behavior as predicted by Eq. 5.5.
Figure 5.15: The measured Stokes $I_{quv}$ vector as a position of compensator angle on the source side. The measurement has been performed on a cloud of particles immersed in a 20 Pa, 8 W argon discharge. A solid line indicates the total intensity; a dashed line indicates the preference for horizontal polarization $Q$, a dotted line indicates the preference for polarization under 45º ($U$), and a dashed-dotted line indicates the preference for the right-handed circular polarization state $V$. This Stokes vector obeys the theoretical behavior predicted by Eq. 5.5.

From the Stokes vector the polarization degree can be calculated. The degree of polarization $P$ is defined by the following relationship:

$$P = \frac{\sqrt{Q^2 + U^2 + V^2}}{I}.$$

An example of the degree of polarization is given in Fig. 5.16. The degree of polarization is plotted as a function of the steppermotor driven compensator azimuth. The degree of polarization changes with the compensator azimuth, which indicates that the compensator imperfections are not determined precise enough, but the oscillation amplitude is small. This indicates that the error is not large. It is also possible that one of the azimuths is wrong. Furthermore, the maximum value is 0.9; this is caused by depolarization due to the cloud of the spherical particles.
Figure 5.16: The resulting polarization degree of the scattered Stokes vector on a collection of spherical particles in an argon discharge (20 Pa, 8 W). Due to the limited number of steps (15) taken with the compensator, the curve is jagged and not smooth. Increasing the number of steps can result in a smoother curve. However this also increases measurement time, which can lead to small deviations caused by e.g. changes in the electrical system of the discharge.

The curve is not very smooth; this is caused by the limited amount of azimuth angles used. Increasing the number of angles can lead to a smoother curve, but might also lead to time influences. The degree of polarization can be used as a check of the calibration. The better the degree of polarization, the more reliable the measured signal becomes. Note that single spherical particles do preserve the degree of polarization, a cloud of non-identical particles does not necessarily do so.

5.7 Conclusions

In this chapter measurements performed with a Mueller matrix ellipsometer are presented. With the MME single particles and clouds of particles in oxygen and argon discharges are diagnosed. Mueller matrix ellipsometry is a very powerful and sensitive diagnostic for the analysis of surfaces. Applied to different surfaces, this diagnostic gives good results.

The main conclusion of this chapter is that particles in discharges struck in oxygen and argon remain spherical. This information is obtained from the Mueller matrix; the matrix remains zero on its non-diagonal elements as one expects for spherical particles. Furthermore, it is possible to compare the measured ellipsometric angle $\Delta$ with the ones calculated with the help of Mie theory.
The diagnostic has several advantages: it measures the full Mueller matrix, the Stokes vector and the polarization degree are measured, and errors are easily visualized. One major drawback of the MME is the use of a stepper motor that limits the real-time monitoring of the plasma processes. The presented measurements indicate that real-time monitoring is still possible if one uses plasma conditions that slow down the etching processes of the particles.

With the technique of MME it is inferred that in an argon discharge the particle size changes very gradually; the observed rate is 0.01 Ås⁻¹. In a reactive environment that can be provided by an oxygen plasma the particle size changes quicker. Measurements on one single spherical particle indicate that the particle is etched with a speed of 0.04 Ås⁻¹ in a low power oxygen plasma.

MME has shown to be a highly sensitive technique; improving the calibration and characterization procedures and improving the measurement speed will result in a diagnostic technique that has monolayer sensitivity.
6. Forward scattering on a single particle

6.1 Introduction

In the last decade the formation, charging, trapping, and behavior of dust in plasmas was extensively studied. Furthermore, a lot of attention was paid to determine the various forces influencing the dust particles and their dynamics. The possibility arose to use the plasma to produce and/or to process particles with interesting physical or chemical properties. However, monitoring plasma processes in which large quantities of powder are processed is extremely difficult. This requires knowledge about both the particle and the different plasma processes. In chapter 4 it has been shown that it is necessary to use size distribution functions to determine the overall scattering properties of a cloud of dust particles. Unlike clouds, measurements on single dust particles directly yield valuable information after comparison with theoretical calculations, e.g. it is much easier to determine properties like size and shape of a single particle. Until now Kortshagen [91] and Homann [29], who both determined the charge on a single particle, have performed measurements on single particles in the field of dusty plasmas. They both determined the charge on single particles. An important input parameter for the calculation of the charge is the particle mass (size). The better the size of the particle is known, the more accurate the charge on the particle can be determined.

The size of particles can be determined in situ and ex situ. Well-known ex situ techniques are SEM, TEM, and optical microscopy. The in situ techniques can be distinguished in three categories[46, 92]:

1. Angle dependent measurements. The measurement of the scattered intensity at a certain angle is compared to another angle, e.g. Plain [58] measured at three different angle 90º±9º. More frequently, the detection system is rotated around the object under investigation and as a result the full scattering diagram is measured, e.g. Rochon [93]. They rotated their nephelometer, which in principle is just a Mueller matrix ellipsometer, around the scattering center. The nephelometer has been used to analyse mixtures of spherical and nonspherical particles.

2. Wavelength dependent measurements. Color measurements can be done; this is based on the Mie parameter x introduced in Eq. 3.18. Different wavelengths are scattered differently. Selwyn [94] shows a calculation of wavelength dependent scattering, and Gebauer [95] has a working three-color rotating compensator ellipsometer setup (488, 514, 633 nm).

3. Polarization sensitive measurements. Polarization measurements are abundant. Often static techniques are used to determine the ratio of horizontal to vertical polarization combined with polarization degree, e.g. [15, 57, 59 - 62]. They all investigated the polarization altering properties of dust particles with optical components at fixed azimuths. Shiratani [60] devised a special optical setup that allowed the determination of the ellipsometric angles. Therefore a threefold detection system has been used which was claimed to have a detectable size limit of 10 nm. Tachibana and Hayashi [24, 25, 63, 64] developed a rotating analyzer ellipsometer to monitor the scattering of carbon particles. To avoid the ambiguity in Δ a quarter-wave plate with fixed orientation is inserted in the setup that allows for the measurement of sinΔ, whereas the rotating analyzer measures cosΔ; this
system operates in two stages. In the previous chapter and in [67], a rotating compensator ellipsometer has been shown that is capable in avoiding the ambiguity in \( \Delta \) within one measurement.

All methods have advantages and disadvantages; all systems will be severely influenced by misalignment. Other (dis)advantages are:

1. Angle dependent measurements can accurately determine the particle size and its refractive index. Furthermore, it is not necessary for this technique to perform destructive measurements. A major disadvantage is the necessity to measure a large angular range; the larger the range the better the final result. However, experimental setups have limited access, and therefore the applicability of these measurements might be limited.

2. Wavelength dependent measurements based on several colors, or on measuring a full spectrum give pretty straightforward data, and directly give information on the particle size and refractive index. On the other hand, aligning optical systems that are using several lasers is not easy, and can be seen as a major drawback for these techniques. Furthermore, spectroscopic sources, especially in the infrared, lack good optical components like polarizers [53].

3. Polarization sensitive measurements have shown to yield reliable data on particle size and refractive index. These techniques often are based on the fact that the object under investigation is changed in an etching or deposition process. In the case that the object under investigation is not changed, these techniques will have large problems in determining size and refractive index. The use of rotating components, as is the case in ellipsometers, enhances the sensitivity considerably.

It is possible to construct diagnostics that are based on more than one method, e.g. spectroscopic ellipsometers can be constructed, or the polarization direction can be changed during angle dependent measurements. This all enhances the diagnostic, and as a consequence, the accuracy of the measurements will improve. It is also possible to combine two independent techniques, e.g. use an angle dependent measurement to determine the size, and use an ellipsometric technique to increase the sensitivity.

In this chapter single particles with a mean size of 12 \( \mu \)m are investigated with the help of an argon laser. The measurements are based on a combination of the first and the third method: the angular scattering profile of a single particle, illuminated by a perpendicular polarized laser, is measured during oxygen plasma operation. In order to relate measured scattering profiles to particle sizes it is necessary to perform simulations. This is treated in section 3. In section 4 the results obtained will be discussed and this chapter starts with a short description of the used setup.

### 6.2 Setup

The experiments are performed in the GEC reactor, see Fig. 6.1. Single melamine formaldehyde particles are injected into the plasma by means of the manipulator arm. In the plasma the particle is ‘caught’ in an artificial particle trap; this trap is an aluminium ring (diameter 2 cm, height 1.5 mm) that is placed in the middle of the powered electrode. The ring locally modifies the electric field and this limits the movement of the particle in the horizontal plane. The ring allows for the creation of small Coulomb crystals in case more particles are injected, but it is especially used to trap one single particle. As a result from the location of the trap and the design of the GEC reactor single particles are localized and can kept at a stable position; sometimes for a very long time (over 15 hours).
This stable-trapping regime permits studying the particle during plasma operation. Therefore the particle is illuminated with an argon ion laser linearly polarized in the direction perpendicular to the horizontal scattering plane.

**Figure 6.1:** Schematical overview of the experimental setup. An argon ion laser is used to illuminate the particles trapped above the ring. A mirror protects the detector for the undeflected light beam; a tube minimizes the scattering of light at the front window.

An optical fibre collects the scattered light in the horizontal scattering plane, passes it through an interference filter (designed for 488 nm, with a bandwidth of 10nm) and feeds it to a photomultiplier. The optical fibre is mounted on a moveable stage that allows continuous scanning of the detection angle in the range of 0° - 15° for forward scattering; it takes approximately 90 s to measure an angular profile. The maximum detection angle is limited by the size of the ports of the GEC reactor. A mirror that is placed inside the reactor to reflect the laser beam, protects the detector for small angles. The fibre, with a square opening of 1 mm² is placed at a distance of 90 cm from the particle and this leads to an angular resolution of 0.06°. Furthermore the moveable stage is placed under an angle (84°) with respect to the undeflected laser beam. In this way the distance between particle and detector is more or less constant and it is not necessary to correct for a possible radial \( r^{-2} \) dependence of the intensity. There is a negligible change in scattering angle when the scattered light is passing through the windows of the GEC cell.

### 6.3 Simulations

In order to relate the recorded scattered intensity to a particle size and a refractive index it is necessary to perform simulations based on Mie theory. Therefore a Matlab program written by Barnett [96] has been adapted. This program has been compared with regard to other simulation codes available at the web site of Wriedt [97], http://imperator.cip-iw1.uni-bremen.de/~fg01/codes2.html, and yielded the same results for a variety of sizes and refractive indices.

One of the problems met in the simulations is to find the ‘best fit’: the calculated scattering profile of a particle with known size and a complex refractive index should exactly match the, noisy, measurement that can be influenced by electrical amplification and offsets. To find the best fit an objective function \( \chi^2 \) is defined:
\[
\chi^2 = \sum_{i=1}^{k} (i_1(\theta_i) - A I_{m,i} + B)^2,
\]

where \(i_1(\theta_i)\) and \(I_{m,i}\) are the far-field scattered intensity and the measured intensity at an angle \(\theta_i\); the coefficients \(A\) and \(B\) represent an amplification factor and an offset respectively. This objective function is minimized with respect to the variables: refractive index, particle size, and an electrical offset and amplification factor. To solve this nonlinear least-squares problem several methods are available [98]. In the program a Nelder-Mead simplex method has been used; this method is a standard option in Matlab.

One of the problems with nonlinear least-squares problems is the occurrence of local minima. The fit routine continues to iterate using solutions that are significantly different from the temporary ‘best’ solution. Sometimes the fit routine does not find a better solution and the found minimum is considered to be the ‘best.’ In practice the best solution is to take a number of different starting points [98] and take the best local minimum that is obtained. The problem with the local minima is illustrated in Fig. 6.2. This figure is a logarithmic grayscale map of the objective function \(\chi^2 + 1\); the 1 is added to avoid that the logarithm becomes infinite. The colors black (0) to white (\(\geq 5\)) indicate the value of the logarithm. For this case two simulations are compared. One is held constant at a size \(r_p = 6.0 \mu m\) and a refractive index \(m = 1.68\), while the other is being varied. The particle size has been varied between \(r_p = 5.4 \mu m\) and \(6.6 \mu m\) with a stepsize of 2.5 nm; the refractive index is varied from \(m = 1.55\) to 1.75 and a stepsize of 0.005.

**Figure 6.2:** A grayscale map of the logarithm of the objective function \(\chi^2 + 1\); the 1 is added to avoid that the logarithm becomes infinite. The colors black (0) to white (\(\geq 5\)) indicate the value of the logarithm. For this case two simulations are compared. One is held constant at a size \(r_p = 6.0 \mu m\) and a refractive index \(m = 1.68\), while the other is being varied. The particle size has been varied between \(r_p = 5.4 \mu m\) and \(6.6 \mu m\) with a stepsize of 2.5 nm; the refractive index is varied from \(m = 1.55\) to 1.75 and a stepsize of 0.005.
local minima can be seen; the program has to discern all these minima and find the best fit. Furthermore, in the plot several minima are connected by ‘tracks’.

Another problem occurs if the start values are not near the real answer; this may lead to solutions that are beyond physical reality, e.g. a very small particle size with a high refractive index. To overcome this problem a large set of different starting values is used in the program. For every value the objective function is calculated. The best fit found, is used as the starting input in the optimization routine. Often the routine has been run more than once as is mentioned above.

A third difficulty is caused when the objective function $\chi^2$ is a non-smooth function. This problem is divided into many different classes of problems and can be attacked by e.g. line search methods. This method searches the minimum of a function along a line in a certain direction. From this minimum a new direction of search is determined and with an iterative procedure the minimum can be found. Associated with this method is the concept of steepest descent, so that the objective function decreases most rapidly to a minimum.

The Nelder-Mead method is a simplex method and thus merely compares function values. A simplex is a set of $n+1$ (equidistant) points in an $n$-dimensional space, e.g. a triangle for $n=2$ and a tetrahedron for $n=3$, see Fig. 3. At the start of the iteration the value of the objective function is determined in all $n$ points, and the point with the highest value (the vertex) is determined. The vertex is reflected in the centroid of the other points and a new simplex is formed. The function value at the new point is evaluated and the process is repeated. Now it is possible that the new point has the highest value and reflection will cause an unwanted oscillation. Then the second-largest value will be used in the reflection procedure. In the end this will no longer work, because all reflection points already exist.

\[ \text{Figure 6.3: The old simplex (solid line) and the new simplex (dashed line). The vertex on the left side has the highest value and is reflected in the centroid spanned by the two other vertices.} \]

Therefore the simplex is contracted, and a new simplex consisting of points halfway along the edge is created. Nelder and Mead suggested a method where irregular simplexes are allowed, and distortions of the simplex are performed automatically in an attempt to take the local geometry of the function into account. According to Fletcher [98] simplex methods are useful when the function values suffer from substantial noise.

### 6.4 Measurements

The angle-resolved scattering measurements are performed in two feed gases: argon and oxygen. Argon is an inert gas and mainly supplies kinetic energy to the particles, while oxygen is reactive and will cause chemical reactions. In an argon plasma it is expected that the particle size remains unchanged if physical sputtering is negligible. Fig. 6.4 shows two
angle-resolved measurements in an argon plasma; the plasma is operated at a pressure of 20 Pa and the RF power amounted 6 W. Squares indicate the first measurement and circles the last. The last measurement is taken approximately two hours after the first, and no remarkable change occurs: the particle size, $r_p = 5.9 \, \mu m$ remains unaltered and so does the refractive index $m = 1.68$. It can be concluded that physical sputtering is unimportant. Also variation of the laser power between 50 mW and 1.6 W does not affect the particle size. The measurements shown are performed at a power of 1.6W.

![Graph](image)

**Figure 6.4:** An angle-resolved scattering measurement on a single particle performed in an argon plasma. The squares indicate the first measurement of a series, while the circles represent the last measurement. The time difference is approximately two hours. The fact that the scattering profile remains the same indicates that the particle size does not change. Simulations indicate a refractive index $m=1.63$ for a particle with a size of $r_p = 5.9 \, \mu m$. The laser power amounted 1.6 W.

In oxygen the situation is different. Oxygen is reactive and it has been used [56, 67] to etch the particle material. It should be noted that there is a large difference between the standard etching of a substrate placed on the electrode and the etching of a free floating particle in a plasma. In the sheath of the powered electrode a high potential on the order of a few hundreds of volts accelerates positive ions towards the surface. High-energy ions, reaching the electrode surface are responsible for sputtering and etching of the material. In contrast, the potential difference between the plasma and a floating particle is much lower, on the order of 1-10 V. Therefore, plasma chemical effects due to low-energy ions and radicals are expected to be most important for microscopic particle etching. In oxygen substantial variations of the scattering signal were recorded already after a few minutes of processing in oxygen. In Fig. 6.5 the time evolution is shown of the angle-resolved intensity scattered by a single particle. The particle has been etched in a 5 W, 20 Pa oxygen plasma.
Figure 6.5: Etching of a single MF-particle in a 5 W, 20 Pa oxygen plasma. The angle-resolved scattering intensity is shown as a function of etching time. The characteristic Mie fringes change and the maxima shift towards higher angles indicating that the particle radius decreases continuously. The measurement was stopped after 160 minutes; at that moment several other particles were observed in the trap.

In the figure the characteristic Mie fringes are clearly visible, and as a function of processing time the maxima shift towards higher angles. This shift can be interpreted as a decrease of particle size. With the help of the simulation program it is possible to determine the time-dependent particle size. As mentioned above simulations are checked several times and this sometimes yields different results. An example of these different results is shown in Fig. 6.6a and 6.6b.
Figure 6.6a: The measurement (hollow squares) performed 10 minutes after particle injection and the result of the simulation (solid line). For clarity 2 out of 3 points are left out. A particle size of $r_p = 6.036 \mu m$ has been deduced; the refractive index is real and amounts to 1.637. The value of the objective function $\chi^2 = 8.2$.

Figure 6.6b: The same measurement (hollow squares) but the simulation started at slightly different input values. This leads to a particle size of $r_p = 5.987 \mu m$; the refractive index is real and amounts 1.717. The value of the objective function $\chi^2 = 12.4$.  

Evaluation of all simulations gives a time-dependent particle size, these results are shown in Fig. 6.7. Sometimes the simulations yields different results, therefore all results with a $\chi^2 \leq 100$ are shown in the plot. The difference in particle radius $r_p$ between two simulations amounts up to 150 nm for the worst case; with respect to the particle size this is just 2.5%.

![Particle Radius vs. Time](image1.png)

**Figure 6.7:** The time-dependent particle size for the measurement in a 5 W, 20 Pa oxygen plasma. All results with a $\chi^2 \leq 100$ are shown. The particle size decreases as a function of time.

![Refractive index vs. Time](image2.png)

**Figure 6.8:** All refractive indices as a function of time. Only the real part is shown.

In the simulations the refractive index is allowed to vary, and it can become complex. This does not happen often; the imaginary part of the refractive index remains zero most of the time. Only in a few cases an imaginary part of the refractive index resulted from the
simulation, whereas the value never was larger than $1.5\cdot10^{-3}$. In Fig. 6.8 the behavior of the real part of the refractive index is shown. It is more or less constant at a value of 1.63 and in the end it appears to change to smaller values.

When the overall behavior of the particle size is taken into account, the size change is easier to distinguish. In Fig. 6.9 all ‘best fits’ are shown; it is evident that e.g. the result for the measurement performed at t=28 min. deviates from the general trend shown in the figure.

![Graph showing particle radius as a function of plasma duration.](image)

**Figure 6.9:** The particle size as a function of time; every point is the ‘best possible’ particle size found in the simulations.

To find an etch rate that is not subjected to noise, a polynomial of 8th order is used to fit through the ‘best fits’; this 8th order polynomial gave the best results. The derivative of the polynomial is taken as etch rate; this is shown in Fig. 6.10. The etch rate decreases from 0.55 nm/s to 0.1 nm/s. The last point in the plot differs from the rest; this is caused by the behavior of the polynomial.

Although these forward scattering measurements are performed at different conditions with respect to chapter 5, it is interesting to note that there are some unexpected differences in the etch rate. Firstly, the etch rate differs by some orders. Partially this can be expected due to the difference in the radio-frequency power, but it does not account for the observed difference. Probably this is implied by the Mueller matrix ellipsometer; it needs a very long time to obtain single datum points and therefore information gets lost. Connected to this is the change of the etch rate: with the forward scattering method it is possible to distinguish different etch rates, which is not possible with the MME.
Figure 6.10: The etch rate of a single melamine formaldehyde particle in an oxygen plasma as a function of etching time. A polynomial (8th order) is fitted through the collection of ‘best fits’ and its derivative is taken. The last point deviates from the rest; this is caused by the polynomial fit.

Figure 6.11: The angle-resolved scattering profile of a single particle measured (hollow squares) directly after particle injection into an oxygen discharge. In the simulation, indicated by the circles the particle radius shrinks with an increase of scattering angle. The simulation resulted in an etch rate of 0.58 nm/s. The particle size $r_p = 6.32 \, \mu m$ and the refractive index $m = 1.62$; chi-square amounted $\chi^2 = 14.9$. 
So far, the particle size is held constant during the simulation of an angular profile. In a measurement however, the particle size actually decreases during the measurement time. This implies that errors are made in the determination of the particle size. Therefore the program has been adjusted to calculate the scattering profile of a particle while it is being etched. In this program it is assumed that the etch rate is constant in time. The extension of the program leads to a drastic increase of the calculation time, and a very good initial guess is needed to keep the simulation time limited to some hours. In Fig. 6.11 the result of the simulation for the first measurement is shown; it leads to a particle size \( r_p = 6.32 \, \mu m \) and a refractive index \( m = 1.62 \), chi-square amounted \( \chi^2 = 14.9 \). Furthermore, the simulation yielded an etch rate of 0.58 \, nm s\(^{-1}\) which is comparable to the etch rate found without adjusting the particle size within the simulation. The same routine also has been applied to the next two measurements, and this led to small but negligible differences. At \( t=4 \) min. the measurement can be specified with a particle size \( r_p = 6.14 \, \mu m \), a refractive index \( m = 1.626 \), an etch rate of 0.39 \, nm s\(^{-1}\), and a chi-square of 28.5. The measurement performed at \( t=10 \) min yielded \( r_p = 5.88 \, \mu m, m = 1.66, \) an etch rate of 0.16 \, nm s\(^{-1}\), and a chi-square of 35. This simulation also has been performed with a reduced data set (only 1 out of 4 measurement points are used) in order to reduce the computational time. Another ‘best fit’ was found: \( r_p = 6.04 \, \mu m, m = 1.63, \) the etch rate equaled 0.2 \, nm s\(^{-1}\), and a chi-square of 2.61. The number of data points obviously influences the value of chi-square. It appears that the etching routine only works in case the program with no etching does not yield good fits. The quality of this fit dictates the final result for the etch rate.

**Figure 6.12:** After 83 minutes of plasma processing it is still possible to fit the measurement with the help of Mie theory. This might imply that the particle remains spherical; the particle has a size \( r_p = 5.3944 \, \mu m \) and its refractive index has become complex and amounts \( m = 1.623 + j \cdot 10^{-5} \), \( \chi^2 = 3.74 \).

The influence of the plasma on the particle is not fully known; it is not obvious that the particle remains homogeneous and spherical during the etching process. However, a
measurement performed at \( t=83 \) min is fitted very easily and this is displayed in Fig. 6.12. Furthermore the value of \( \chi^2 \) is the best of all simulations, \( \chi^2 = 3.74 \). This implies that the Mie theory is still applicable to the measurements. This might be an indication that the particle is still spherical and that its material is still homogeneous.

The decrease of the etch rate is unknown. As the plasma changes the particle size, it might also change the particle composition, e.g. deposit a passivation layer, change the refractive index et cetera. Therefore some simulations have been performed. The scattering profile of a particle which had a coating layer has been calculated. The core of the particle in all simulations was a 6.2 \( \mu \)m-sized particle with a refractive index of 1.64, comparable to the results of the measurements. On top of this a shell of different refractive indices and sizes was put; the refractive indices used are 1.2, 2.0, and 1.64-0.1i, and these layers had thicknesses of 1, 5, 10, and 50 nm. In Fig. 6.13 a scattering profile of a 6.25 \( \mu \)m-sized particle with real refractive index is compared to the same particle with a complex refractive index.

![Graph](image)

**Figure 6.13:** The angular profile of a naked (dashed) and a coated (solid) particle. The naked particle is a 6.25 \( \mu \)m-sized particle with a refractive index equal to 1.64. The coated particle has a 6.2 \( \mu \)m core with a refractive index 1.64, and on top of that a shell of 50 nm, with refractive index 1.64-0.1i.

The result of the simulation of Fig. 6.13 is used as input into our algorithm. By comparing the simulation and its fit, it might be possible to pinpoint the mechanism that decreases the etch rate. Unfortunately, the fit does not provide a very good simulation for the 50-nm shell. The fitting results of the other coated particles are quite irregular:

1. Layers of up to 10 nm give good results for the refractive indices 1.2, and 1.64-0.1i; the obtained refractive index is within 1% and the particle radius differs by 100nm at most.
2. The particles with a \( m=2 \) shell are difficult to simulate, and give same plots like Fig. 6.13. Also the absorbing particles with a coating larger than 10nm are hard to simulate.
As a consequence it is difficult to pinpoint the creation of a reaction layer as the limiting mechanism. To solve this problem it might be necessary to enhance the angular range of the diagnostic; during the simulations it has been observed that an angular scattering profile becomes more unique with increasing angular range. Furthermore, the combination of this diagnostic with the Mueller matrix ellipsometer that measures the scattering under 90° might increase the sensitivity for changes in the refractive indices and the number of layers. To that extent, it is necessary to increase the speed of the simulations because the simulation of coated particles consumes too much time.

![Graph showing intensity vs angle](image)

**Figure 6.14:** The angular profile of the simulated coated particle and the ‘best fit’ to that simulation, assuming that the particle consists of a single layer. The results of the fit are a refractive index of 1.64 and a particle size of 6.35 µm.

A parametric research has also been performed; changing the plasma parameters can influence the etching process. Unfortunately this also changes the stability of the particle trap, and therefore the changes only cover a very limited area. The etch rate was found to increase both with pressure and radio-frequency power [99].

### 6.5 Conclusions

The measurement of the angular scattering profile of a particle gives very accurate particle size and refractive index information. With this technique the etching process of a particle in an oxygen plasma has been monitored very accurately during its treatment. During the oxygen treatment the particle size changes, while the angle-resolved scattering profiles indicate that the particle remains spherical. Furthermore, it has been shown that it is no problem that the particle size changes during the measurement of an angular profile; as a result still a particle size can be obtained. Increasing the totally measured angular range can further enhance this technique, as the scattering profiles become more unique with increasing scattering angle. The forward scattering measurements have been demonstrated
as a very sensitive diagnostic, which result in more useful data than the ellipsometer shown in chapter 5. However, an enhanced, faster, ellipsometer combined with the angle-resolved measurement technique will result in an extremely sensitive particle surface diagnostic that is capable of determining the deposition of thin layers of e.g. catalytic materials.
7. The thermal balance

7.1 Introduction

In this chapter the thermal power balance for powder particles is treated; this balance takes several energy fluxes arriving at and leaving from the particle surface into account: kinetic energy of ions and electrons, ion recombination energy, radical association energy, thermal conduction, radiation and chemical reaction heat. Due to these fluxes, an internal particle temperature $T_p$ is settled and its determination yields valuable information about all these different fluxes.

Daugherty [100] has reported one of the few efforts in this direction. He was able to measure the temperature of manganese activated magnesium fluorogermanate particles in the afterglow of an argon plasma of 40 Pa and 50 W. To this purpose, the decay time of the phosphorescence of the particles was measured after extinction of the argon plasma. As has been shown by Wickersheim [101] the decay time is temperature dependent. Daugherty's measurements resulted in a temperature of $410 \pm 10K$ for the particles. In other fields e.g. in fluid mechanics, temperature measurements yield valuable information about combustion processes. Coppeta [102] has shown that dyes like Rhodamine B can be used to measure temperatures of thermal plumes. Justus et al. [103] have used a fluorescein dye to measure the heating of condensed phase materials by compressional shock waves.

In this chapter it will be shown that the spectral profile of the fluorescent emission of melamine formaldehyde powders which have been volume dyed with Rhodamine B (MF/RhB) is temperature dependent. These particles have been used to measure real time and in-situ, the internal temperature of these particles while they are suspended in RF plasmas in argon and oxygen. These two gases are used because they differ in behavior: argon is inert and supplies mainly kinetic energy, while oxygen is reactive and supplies, in addition, also other energetic contributions like chemical reaction energy. Measurements of the internal temperature of the particle combined with data on gas temperature, electron density and electron temperature will be shown to give a good insight in the energy fluxes from plasma to dust particles and, thus, in plasma-particle interactions.

This chapter is divided in three parts. In the first part diode laser measurements of the gas temperature are presented. Subsequently, Langmuir probe measurements are shown that have been used to measure the electron temperature. In the last part the internal particle temperature measurements are introduced followed by a discussion based on the thermal power balance. This chapter starts with a short introduction of the setup. Parts of this chapter are submitted for publication [104]

7.2 Setup

In order to fully determine the thermal power balance it is necessary to determine gas temperature, electron temperature, electron density and the internal particle temperature. In Fig. 7.1 the used setup is shown; all experiments are performed in the GEC cell. The gas temperature has been measured by means of a diode laser system (Environmental Optical Sensor Inc. LCU-2010-M, ECU-2010-M, SN00194 diode) with a line width of 5
MHz. This system has been used to measure the line width of the argon 1s₅ metastable absorption line (811.531 nm). The intensity of the system before and after transmission through a plasma is recorded using a BPW34 photo diode. The system is operated using a diode laser.

Figure 7.1: A schematic overview of the setup used for the temperature measurements. The diode laser is used to measure the absorption profile of the argon gas and subsequently the temperature of the gas. The argon laser is used to excite the volume dyed MF/RhB particles in order to measure a particle temperature. The Langmuir probe system is used to measure the electron temperature, the electron and ion density, and the plasma and floating potential.

Figure 7.2: A typical plot of the transmitted intensity Iₗ (hollow squares) in an argon plasma operated at 20 W, 20 Pa. The drawn line is the fitted intensity assuming no absorption. The wavelength of the used diode laser is varied linearly around its central wavelength (811.531 nm).
neutral density filter to reduce the laser power so that stimulated emission can be neglected. A typical absorption measurement is shown in Fig. 7.2; the squares indicate the measured intensity in a 20 Pa, 20 W argon plasma and the solid line is the fitted intensity without any absorption. The measurement is plotted around the central wavelength of 811.531 nm; the measurement needs to be transformed to the absorption profile as will be explained in the next section. The absorption profile is shown in Fig. 7.3 and from the width of the absorption curve (1.77 pm) for this example a gas temperature of 98 °C can be determined.

![Figure 7.3](image.png)

**Figure 7.3:** The optical depth (squares) as a function of the wavelength shift with respect to the central wavelength of the diode laser. Analysis (solid line) of this absorption profile yields a Doppler broadening of $\Delta\lambda_D = 1.77$ pm which results in a gas temperature of $T = 98$ °C.

A commercial Langmuir probe system (SmartProbe, Scientific Systems, [105]) has been used to measure the electron density $n_e$ and the electron temperature $kT_e$. Furthermore the system measures the plasma potential $V_p$, the plasma floating potential $V_f$, the ion density $n_i$, the electron energy distribution function (EEDF), and the Debye length $\lambda_D$. The SmartProbe is an automated Langmuir probe system mounted on an autolinear drive (stroke 250 mm). It consists of a cylindrical conducting tungsten wire (length 10 mm, diameter 0.4 mm) that can be inserted into the plasma; the wire is mounted on an alumina shaft. In the plasma the wire is DC biased to draw current from the plasma. A current $I$-voltage $V$ characteristic is measured and analysis of the $I$ - $V$ characteristic yields the plasma parameters. The probe is equipped with a high and a low frequency plasma potential sensor. The high frequency sensor compensates for the time dependent variation of the plasma potential caused by the RF driving voltage. The low frequency sensor is allowed to float at the plasma floating potential and is used to track and to eliminate any low frequency DC shifts in the plasma potential. Furthermore the Langmuir probe system is equipped with a computer program ‘SmartSoft’ that takes care of the measurement and the analysis.
For the measurements of the internal temperature of the particles we have used melamine formaldehyde (MF) spheres, which are dyed throughout the volume with Rhodamine B (MF/RhB, supplier: Microparticles GmbH Berlin). The spheres have an original diameter of $2r_p = 1.2 \, \mu m$, a specific mass density of $\rho = 1.51 \, g/cm^3$ and a real refractive index of $n = 1.68$. The mass fraction $m_f$ of the dye in the spheres is less than 1%. Rhodamine B has a boiling point of 210 °C; heating the particles above this temperature leads to a degradation of the dye.

An argon ion laser (Coherent Innova 70, operated at 514 nm and 28 mW) was used to excite the dyed particles. The resulting fluorescent emission has been recorded using an EG&G optical multichannel analyzer (model 1461). The OMA system has been corrected for the sensitivity of the solid state detector (EG&G model 1420) using a tungsten ribbon lamp.

For calibration purposes, the spectral behavior of the dyed particles has been recorded as a function of temperature after mixing the particles with oil (Balzers, F3, turbo molecular oil). The mixture was heated from room temperature to 210 °C. A Fluke 8024A multimeter with thermocouple has been used to monitor the temperature of the mixture. The accuracy of the temperature measurements is 5 K. As indicated by Guilbault [106] solvent broadening of the emission curves can occur for dyes. However, in our case the dye is ‘solved’ in the particle material and therefore the surrounding of the dye is the same for all cases, whether the particles are suspended in oil or in the plasma. It has also been checked whether scattering of the oil influences the measured spectrum; this is shown in Fig. 7.4.

![Figure 7.4](image)

**Figure 7.4:** The scattering of oil and air with respect to the fluorescent emission and the scattering from the particle emulsion.

It is obvious that the scattering of oil does not influence the calibration curves. In Fig. 7.5 a few temperature calibration curves are shown for the MF/RhB particles. The calibration curves show that the spectral profile of the fluorescent emission depends on the temperature.
One can clearly see that as a function of temperature the curve broadens and the peak intensity decreases. This makes it possible to determine the temperature $T_p$ of particles suspended in the plasma without making use of the absolute intensity. This is very convenient: several processes and plasma parameters may hamper reliable measurements of the absolute intensity. The number of trapped particles is not always constant, photo bleaching can occur due to laser irradiation, UV lines of the plasma can degrade the dye, and further processes in the plasma like etching and sputtering can change the particle and the dye.

Since a laser is used for illumination and excitation of the dust particles in the plasma, the influence of laser heating to the particle has to be estimated. The laser is operated at a power of $P_l = 28 \text{ mW}$ and has a beam diameter of $d_l = 4 \text{ mm}$. Only the Rhodamine B in the particle will absorb light; the mass fraction of the dye in MF is $m_f = 1\%$. The absorption of Rhodamine B depends on the excitation wavelength; for 514 nm the absorption relative to the maximum at 550 nm is given by the absorption efficiency $Q_A$, $Q_A = 0.35$. Also the quantum yield for fluorescence radiation is important; each photon emitted carries away energy from the particle. In ethanol the yield is $\phi = 0.69$ according to Guilbault [106]. Applying this to our particles gives an emission efficiency of $Q_E = 0.6$ with respect to the absorbed energy. The laser power which is absorbed by the MF particle thus amounts $P_l (2r_p/d_l)^2 (m_f)^{2/3} Q_A (1 - \phi) = 51 \text{ pW}$.

The particles have a mass of $m = 8 \cdot 10^{-13} \text{ kg}$ and the specific heat capacity of the MF material is taken to be roughly $10^3 \text{ Jkg}^{-1}\text{K}^{-1}$. This results in a heat capacity of $0.8 \text{ nJK}^{-1}$ for each particle. The particle temperature $T_p$ will change at a rate of $\partial T_p/\partial t = 63 \text{ mKs}^{-1}$. This ultimately results in an upper limit for the temperature increase of 0.63 K for our measurement time of 10s. Therefore we estimate the influence of laser heating on the measurements to be negligible.
A typical measurement in a 20 Pa, 42 W argon plasma is shown in Fig. 7.6. With the help of the calibration curves, a temperature of the particles of \((19 \pm 1)10 \, ^{\circ}C\) is obtained. In Fig. 7.7 the residue of measurement curve and calibration curve is shown.

![Figure 7.6](image)

**Figure 7.6:** A typical measurement (squares) of the RhB-doped particles suspended in a 20 Pa, 42 W argon plasma. Also a calibration curve is shown (circles). A particle temperature of \((19 \pm 1)10 \, ^{\circ}C\) is determined.

![Figure 7.7](image)

**Figure 7.7:** The residue of the measurement curve and the calibration curve shown in the previous figure.
7.3 Gas temperature measurements

7.3.1 Theory

The transmission of a laser beam through a plasma is given by:

\[ I_b(\lambda) = I_u(\lambda) \exp(-\tau_{ab}(\lambda)), \quad (7.1) \]

where the optical depth \( \tau_{ab}(\lambda) \) equals the integral of the absorption coefficient \( \kappa_a(\lambda) \) over the “line of sight”:

\[ \tau_{ab}(\lambda) = \int_a^b \kappa_a(\lambda) dx. \quad (7.2) \]

This absorption coefficient is given by

\[ \kappa(\lambda) = \frac{\lambda_0^4 A}{8\pi c} g_{4p} \left( \frac{g_{4s}}{g_{4p}} \frac{n_{4p}}{n_{4s}} \right) n_{4s} \phi(\lambda), \quad (7.3) \]

with \( n_{4s,p} \) and \( g_{4s,p} \) the density of the lower (upper) state and its statistical weight, \( c \) the speed of light, \( \lambda_0 \) the central wavelength (811.531 nm) of the transition, and \( A \) the transition probability for spontaneous emission \( (0.331 \cdot 10^8 \text{ s}^{-1}) \) from the 4p to the 4s state. The area of the absorption profile \( \phi(\lambda) \) is normalised to 1. The term between brackets represents the stimulated emission and this term is only important if the ratio of density per statistical weight of the upper state \( n_{4p}/g_{4p} \) becomes comparable to the ratio of the lower state: \( n_{4p}/g_{4p} \). However, low laser intensity will not lead to an important population of the upper state. In this case after neglecting the term between brackets, Eq. 7.3 directly links the absorption coefficient to the density of the 4s state.

Besides the 4s density, also the gas temperature can be measured. The width of the optical depth is mainly determined by Doppler broadening. This broadening is determined by the thermal motion of the atoms and results in a Gaussian shaped absorption profile with a FWHM linewidth that is given by [108, 109]

\[ \Delta \lambda_D = \lambda_0 \sqrt{\frac{8 \ln 2 k_B T_g}{m_{Ar} c^2}}, \quad (7.4) \]

where \( T_g \) the gas temperature and \( m_{Ar} \) the mass of an argon atom. The two other broadening mechanisms are Stark broadening and Van der Waals broadening. Stark broadening results from the interaction of bound and free electrons and results in a Lorentzian absorption profile with a FWHM of [110]:

\[ \Delta \lambda_s = 2 \cdot 10^{-22} n_e \left[ 1 + 5.5 \cdot 10^{-6} \alpha_e \sqrt{n_e} \left( 1 - 6.8 \cdot 10^{-3} \frac{\sqrt{n_e}}{T_e} \right) \right], \quad (7.5) \]
with $\alpha$ and $w$ the ion broadening parameter (0.021, [111]) and the electron impact parameter (5.1 pm) respectively. The Stark broadening, $\Delta \lambda_s = 10^{-17}$ m, is negligible for typical conditions in our GEC reactor ($T_e = 11600$ K, $n_e = 10^{16}$ m$^{-3}$). Van der Waals broadening results from the interaction between atoms and molecules and can be estimated by

$$\Lambda \lambda_V = \gamma n_a,$$

(7.6)

where $\gamma$ the Van der Waals or pressure broadening coefficient ($5 \cdot 10^{-27}$ nm/m$^{-3}$, [112]) and $n_a$ the neutral particle density given by the ideal gas law. A maximum broadening of 0.05 pm is found and, like the Stark broadening, Van der Waals broadening is negligible.

### 7.3.2 Gas temperature in argon

In Fig. 7.8 the gas temperature is shown as a function of RF power for four different feed gas pressures; all measurements are performed at a height of 6 mm.

![Figure 7.8: The argon gas temperature as a function of RF power for four different pressures. The measurements performed at 5 and 10 Pa are not reliable above 30W of RF power, and as a consequence are left out.](image)

The gas temperature rises with RF power and is independent of pressure. Note that the measurements performed at 5 and 10 Pa are not reliable above 30 W of RF power. At these values, the level of the background signal fluctuated and sometimes this fluctuation hampered in determining the full absorption profile accurately. Therefore the analysis possibly yielded wrong results and as a consequence the measurements are left out in Fig. 7.8. The density of the 4s state can be found from integration of the area under the absorption profile. This is depicted in Fig. 7.9.
The thermal balance

Figure 7.9: The $4s$ density as a function of RF power for four different feed gas pressures (5 Pa, 10 Pa, 20 Pa, 40 Pa are indicated by squares, circles, up-triangle, and down-triangle respectively). The density increases with RF power and decreases with pressure. All measurements are performed on the same height, namely 6 mm.

The metastable density measurements, depicted in Fig. 7.9, do not fulfil our expectations. It is expected that the metastable density increases with increasing pressure; the neutral density increases and loss mechanisms like diffusion become less important. However, the electron temperature decreases with pressure, and this might influence the $4s$ density. Jonkers [112] has observed similar behavior of the $4s$ density in an QL-lamp filled with argon. McMillin [113] performed relative absorption measurements on a GEC cell with an electrode distance of 2.54 cm. These measurements show that the axial profile changes as a function of pressure; at a pressure of 13.3 Pa the profile is nearly symmetric and it peaks near the center of the discharge. With increasing pressures, the profile becomes more asymmetric and the peak approaches the electrode. As the measurements are relative, no numbers are given concerning changes in the metastable density; McMillin mentions previous measurements in similar conditions where the argon metastable density is in the order of $10^{17}$ m$^{-3}$. Unlike McMillin, we operate our GEC cell with an electrode distance of 6.35 cm, in order to allow for the particle injection and this can lead to variations in the observed metastable densities.

An axial scan is made to obtain the temperature profile as a function of height above the RF electrode. The vertical scanning range is limited due to a presence of a tube on the reactor. This tube minimizes the scattering of the laser on the window, but also limits the scan height. Therefore measurements have been performed from the powered electrode to 20 mm above the electrode. The results of the gas temperature measurements are shown in Fig. 7.10; the measurements are performed in a 20 Pa, 20 W argon plasma. Furthermore the metastable density has been determined; this is shown in Fig. 7.11. In both figures, the position of the glow-sheath transition can be determined. The gas temperature reaches the highest temperature at the glow-sheath transition region, where the plasma is the most active; towards the cooled electrode and deeper into the glow the gas temperature
decreases. The metastable density shows a similar but more pronounced behavior. No lateral absorption measurements are performed, and thus no Abel inversion is necessary. Therefore we have to assume a profile of the metastable density and the temperature distribution. We have assumed that both profiles are flat. McMillin’s measurements indicate that this is approximately the case; sometimes there is some influence of the ground shield which locally perturb the metastable density profiles.

**Figure 7.10:** The gas temperature as a function of height in an argon RF plasma operated at 20 W and 20 Pa. The gas temperature peaks at the glow-sheath transition region and becomes lower towards the cooled electrode and further into the glow.

**Figure 7.11:** The metastable density as a function of height above the powered electrode. The density peaks at the sheath-edge and diminishes towards the glow and to the cooled and powered electrode.
7.4 Langmuir probes

7.4.1 Theory

Objects contacting a plasma, like a Langmuir probe, are charged negatively due to difference between ion and electron mobilities. The plasma compensates for the loss of electrons to the probe by developing a sheath between the plasma and the probe tip. When a varying voltage is applied to the Langmuir probe a net current to the probe tip is measured. A current $I$ - voltage $V$ characteristic is measured and analysis of the $I$ - $V$ characteristic yields the plasma parameters; a typical $I$ - $V$ curve is shown in Fig. 7.12.

![Figure 7.12: An example of a measured V-I characteristic (solid line) with a Langmuir probe and two theoretical fits (dashed and dotted line); the fits are obtained using a simple and a more advanced theory, see the text for more details. Three different regions are indicated: 1. ion saturation regime, where the total current is determined by the ions, 2. electron saturation regime, where the total current is determined by electrons and negative ions, and 3. electron retardation regime, where the total current is determined by electrons and positive and negative ions. This measurement was performed in a 20Pa, 40 W argon plasma with an electron temperature of 1.2 eV.](image)

Three main regions [105] can be distinguished in the curve:

1. The electron saturation region. In this region the probe is biased positively with respect to the plasma potential. Negative ions and electrons are attracted to the probe and electron saturation occurs.

2. The electron retardation region. The probe is biased negatively with respect to the plasma potential and it attracts electrons, which are energetic enough to overcome the potential barrier. If the electron distribution is in thermal equilibrium the
electrode current is exponential with respect to the applied voltage and the slope of the exponential region yields the electron temperature. At the point where no net current is measured, a potential has developed on the probe known as the floating potential $V_f$.

3. The ion saturation region. For increasingly negative potentials with respect to the plasma potential a point is reached where no electrons reach the probe and only positive ions are collected. This region yields the ion number density in the plasma.

The measured $I$ - $V$ characteristic can be analysed with a simple probe theory or by the more advanced Laframboise theory that takes the expansion of the sheath around the probe tip into account [105].

In the simple probe theory, the electron temperature is calculated by taking the current measured at the plasma potential and dividing it by the integral of the $I$-$V$ curve from the floating potential $V_f$ to the plasma potential $V_p$:

$$\frac{1}{k_B T_e} = \frac{I(V_p)}{V_p} \int_{V_f}^{V_p} I(V) dV.$$  \hspace{1cm} (7.7)

The plasma potential can be found by looking at the first and second derivative of the current with respect to the applied voltage: the first derivative has a maximum, and the second derivative is equal to zero at the plasma potential. Once the electron temperature is known, from the current at the plasma potential also the electron density can be calculated:

$$n_e = \frac{I(V_p)}{A_p} \left( \frac{2\pi m_e}{e^2 k_B T_e} \right)^{1/2},$$  \hspace{1cm} (7.8)

where $A_p$ is the area of the probe, and $m_e$ is the mass of the electron. The well-known Debye length can be calculated from electron density and electron temperature according to

$$\lambda_D = \sqrt{\frac{\epsilon_0 kT_e}{e^2 n_e}}.$$  \hspace{1cm} (7.9)

Laframboise has developed a more advanced theory; this theory takes the expansion of the probe sheath into account. The probe sheath expands as a function of the applied voltage across the probe, and thus influences the measured current. As a result, the measured plasma parameters are altered. The expansion of the sheath width with the applied voltage can be approximated by:

$$d_s = \lambda_D \sqrt{\chi},$$  \hspace{1cm} (7.10)

where

$$\chi = \frac{V - V_p}{k_B T_e}.$$  \hspace{1cm} (7.11)
and $V$ is the applied voltage; Eq. 7.10 is only valid above the plasma potential. Furthermore, Laframboise developed a theory, which can be used to calculate the ion and electron currents to the Langmuir probe as a function of applied voltage for a range of different Debye $\lambda_D$ and probe radii. The currents can be condensed into the following equations:

\begin{align}
I_e &\approx \alpha_e \chi_e^{\gamma_e} I_{0e}, \\
I_+ &\approx \alpha_+ \chi_+^{\gamma_+} I_{0+},
\end{align}

(7.12)

where $I_{0e}$, $I_{0+}$ are the thermal fluxes of electrons and ions respectively, $\gamma_e$ and $\gamma_+$ are sheath expansion factors, depending on $r_p/\lambda_D$ that are approximately equal and $\alpha_e$ and $\alpha_+$ are factors that also depend on $r_p/\lambda_D$.

To find the sheath expansion factor $\gamma_e$ and $\alpha_e$ it is necessary to fit the electron current in the electron saturation region:

\begin{align}
I_e &\approx \alpha_e \left[ \frac{V - V_p}{k_B T_e} \right]^{\gamma_e} I_{0e}.
\end{align}

(7.13)

To obtain the plasma potential graphically we intersect the extrapolated electron saturation current with the extrapolated exponential retarded electron current; this is shown in Fig. 7.13. This method is known as ‘intersecting slopes.’

The intersecting slopes technique can be represented by:

\begin{align}
I(V_p) \exp \left( \frac{V_p}{k_B T_e} \right) = \frac{I(V > V_p)}{\alpha_e \left( \frac{V - V_p}{k_B T_e} \right)^{\gamma_e}.}
\end{align}

(7.14)

and from this equation a more accurate plasma potential can be calculated. This leads to a more accurate value for the current and hence to a more accurate value for the electron density.

The ion density can be determined in a similar manner; at a large negative voltage the ion thermal current $I_{0+}$ is determined by

\begin{align}
I_{0+} = \frac{I(V)}{\alpha_+ \chi_+^{\gamma_+}}.
\end{align}

(7.15)

The value for the ion thermal current is necessary to determine the ion density $n_+$:

\begin{align}
n_+ = \frac{I_{0+}}{A_p \left( \frac{2\pi m_i}{e^2 k_B T_e} \right)^{\frac{3}{2}}}. \quad (7.16)
\end{align}

Note that in the sheath region this relation is no longer valid.
Figure 7.13: The intersecting slopes technique applied to an experimental \( I - V \) curve. A straight line (dashed) is drawn through the current curve and the line is extrapolated until it intersects the line that is drawn at the end of the exponential part of the \( I - V \) curve. Finally this leads to a better determination of the plasma potential \( V_p \) and thus to a better determination of the electron density \( n_e \).

7.4.2 Langmuir probe measurements

In a 20 Pa, 70 W argon plasma, a Langmuir probe has been used to measure the height dependence of several plasma parameters. To facilitate these measurements, it was necessary to connect the Langmuir probe system to the GEC cell via a flexible bellows. Due to this bellows, the probe height could be varied in the plasma. Unfortunately, the bellows also introduced a small tilt in the probe. The tilt, which is equal to 0º at a height of 0.8 cm, amounts to 5º at a height of 2.1 cm; the measurements have not been corrected for the tilt.

A measurement of the electron temperature as a function of height is shown in Fig. 7.14 the Langmuir probe measurements were started in the glow, at a height of 2.1 cm. At that height electron temperatures have been measured in the order of 1 eV. Gradually the probe has been moved towards the electrode surface thereby going from glow via presheath to the sheath. As a result the measured pseudo electron temperatures increased. However, in the sheath – presheath region the probe theories are no longer valid because there is a lack of thermalizing collisions and the results do not have to be correct. However, Bradley [114] has performed measurements in a magnetron discharge with a Langmuir probe and combined this with modeling. His measurements show a similar behavior as shown in Fig. 7.14.
Figure 7.14: The electron temperature as a function of height above the powered electrode. The transition glow – presheath is indicated. Below this transition the measurements should no longer be trusted; in fact a pseudo electron temperature is measured. The measurement is performed in a 20Pa 70W argon plasma.

Figure 7.15: The electron (squares) and ion (circles) density as a function of height above the powered electrode in a 20 Pa 70 W argon plasma. Ion measurements performed in the glow-sheath transition region are left out, as Eq. 7.16 is no longer valid.
In Fig. 7.15 the measured densities are shown; the electron and ion density both show the same behavior; the densities decrease towards the electrode. Striking is the difference between electron and ion density; in inert gases like argon one expects equality of electron and ion densities, but unfortunately this is not the case. A possible cause is the analysis technique; the measurements have been analyzed using the advanced, intersecting slopes technique because this gave the best visual results. However, analysis of the measurements using the simple probe theory changes the results of the measurements and the electron density is plasma parameter that is affected the most. With the simple probe theory, the difference between electron and ion density reduces to 10% or less. Furthermore, the difference might be caused by impurities in the reactor, which can be introduced in several manners, and as a result the plasma can become partially electronegative. Possible sources of impurities are the dust particles that are used in this study, feed gases, pump oil, reactor material, and probe material.

The presence of the impurities led to a premature end of the measurements because of a contamination layer was formed on the probe tip; this could not be removed with the SmartClean option, and also an oxygen plasma was not capable thereof. The formation of the contamination layer could be controlled in the glow region with the SmartClean option, but not in the sheath region.

In Fig. 7.16 the plasma and the floating potential are shown which are constant in the glow and change with decreasing height. In Fig. 7.17 the measured ion current to the probe is shown.

**Figure 7.16:** The floating $V_f$ and the plasma potential $V_p$ as a function of height above the powered electrode.
The thermal balance

Figure 7.17: The ion current as a function of height above the powered electrode.

To get an idea about the typical plasma parameters at the operating conditions of the GEC cell, Langmuir probe measurements have been performed for various discharge powers. The probe was positioned in the glow of the plasma to avoid the formation of a contamination layer; the actual height was 2.2 cm. For increasing discharge powers it has been observed that the electron temperature in the argon plasma drops as is expected, see Fig. 7.18. A possible explanation might be the $\alpha \rightarrow \gamma$ transition as described by Belenguer [115]; this transition has been observed in the used radio-frequency plasmas. All measurements are performed twice, where one measurement consisted of 50 samples, and accordingly one can get an idea of the reproducibility. With increasing power, the electron and ion density increase as is indicated in Fig. 7.19 and with a higher electron density the electron temperature drops.
Figure 7.18: The electron temperature as a function of RF power in a 20 Pa argon plasma; the measurements are performed at a height of 2.2 cm above the electrode.

Figure 7.19: The electron and ion density as a function of RF power in a 20 Pa argon plasma, at a height of 2.2 cm above the electrode.
In Figs. 7.20 and 7.21 the floating and plasma potential and the ion current are shown respectively.

**Figure 7.20:** The floating and the plasma potential as a function of RF power in a 20 Pa argon plasma as measured in the glow of the plasma. The measurements were performed at a height of 2.2 cm.

**Figure 7.21:** The ion current to the probe as a function of RF power in a 20 Pa argon plasma measured at a height of 2.2 cm.
7.5 Internal particle temperature

7.5.1 Thermal balance of powder particles confined in a plasma

In practical applications of plasma-particle interactions, it is important to know the energy fluxes towards and from particles which result in a certain temperature of the particles. The particle temperature $T_p$ affects elementary processes like adsorption, desorption, and diffusion as well as chemical reactions at the particle surface. For example, the thermal balance of a particle influences its surface properties as stoichiometry, microstructure etc. [68, 116, 117].

The thermal balance of the particles can be written as an equality between the thermal influx $Q_{in}$, the temporal derivative of the particle enthalpy $H_p$ and the thermal outflux $Q_{out}$:

$$Q_{in} = \dot{H}_p + Q_{out}. \quad (7.17)$$

In the stationary situation of the particle being suspended in the plasma, $H_p = mc \frac{dT_p}{dt} = 0$.

The fluxes $Q_{in}$ and $Q_{out}$ are the surface integrals of the related energy flux densities $J_{in}$ and $J_{out}$, respectively, over the particle surface $A_p$: $Q_{in} = \int J_{in} dA$, $Q_{out} = \int J_{out} dA$. In the following, the energy flux densities will be discussed in more detail. In general, the total energy influx $J_{in}$ is the sum of the influxes due to the kinetic energy of electrons ($J_e$) and ions ($J_{ion}$), the energy which is released when a positive ion recombines at the surface of the floating particle ($J_{rec}$), the energy $J_{ass}$ which is supplied when two gas phase species (e.g. O-atoms) associate into one another gas phase species at the surface (e.g. O$_2$-molecule) of the particle and the energy $J_{chem}$ which is released if a chemical reaction occurs between a gas phase species and the surface:

$$J_{in} = J_e + J_{ion} + J_{rec} + J_{ass} + J_{chem}. \quad (7.18)$$

Contributions to the energy influx due to laser irradiation and plasma radiation can be neglected in our case as discussed above and because of the relatively low temperature.

The kinetic energetic contributions ($J_e$, $J_i$) of the electrons and ions, respectively, are products of the particle fluxes and the mean kinetic energy and may be obtained by:

$$J_e = n_e \sqrt{\frac{kT_e}{2\pi m_e}} \exp\left\{ \frac{-e_0 V_{bias}}{kT_e} \right\} \cdot 2kT_e, \quad (7.19)$$

$$J_i = n_i v_{amb} e_0 (V_{pl} - V_\beta) = n_e \sqrt{\frac{kT_i}{m_i}} \exp\{-0.5\} \cdot e_0 (V_{pl} - V_\beta), \quad (7.20)$$

where we have approximated the ambipolar diffusion velocity $v_{amb}$ in Eq. (7.21) by the Bohm velocity [118]

$$v_\beta = \sqrt{\frac{kT_i}{m_i}} \exp(-0.5). \quad (7.21)$$
Under low pressure conditions \((p < 50Pa)\) the Bohm equation is applicable, because in the sheath almost no collisions occur. The Bohm equation yields the ion flux by knowing the electron density \(n_e\) that equals the ion density \(n_i\) at the sheath edge. It should be mentioned that the expressions for the mean electron energy of \(2kT_e\) in Eq. (7.20) are only valid for a Maxwellian electron energy distribution function (EEDF). If another EEDF holds, one has to modify this contribution. However, in the floating potential \(V_f\) which is the particles potential, the influence of different EEDF’s concerning \(J_e\) is negligible [116]. In case of particles suspended in a plasma, the electron and ion currents towards the particles are equal \((j_e = j_i)\) and the released recombination energy flux \(J_{rec}\) is:

\[
J_{rec} = j_e \cdot (E_i - \varphi),
\]

where \(E_i\) is the ionization energy, which is for argon 15.7eV. \(\varphi\) is the work function which may be important for metallic particles. In principle, equation (7.22) should be corrected with the difference between the adsorption energy of the ion and the desorption energy of the resulting neutral, but this contribution is rather low.

The energy influx \(J_{ass}\) by atom recombination (association) is described by:

\[
J_{ass} = \Gamma_0 \cdot n_o \cdot \frac{8kT}{\pi m_o} E_{diss},
\]

where \(\Gamma_0\) is the association probability of O-atoms on the particle surface, \(T_g\) is the gas temperature, \(n_o\) is the density of O-atoms, \(m_o\) is the mass of O-atoms, and \(E_{diss}\) is the dissociation energy of O\(_2\) molecules. Little is known of the association probability \(\Gamma_0\); it depends on the O-atom surface coverage ratio and the sticking coefficient. A value of 0.05 for \(\Gamma_0\) has been estimated for a similar case [119]. For an estimation of the maximum contribution of this effect, we will take \(\Gamma_0 = 0.1\).

The exothermic chemical reaction (i.e. combustion) energy can be estimated from the etch rate \(r_p\), the particle material density \(\rho\), and the average specific combustion enthalpy gain \(h_{comb}\):

\[
J_{chem} = r_p h_{comb}.
\]

The outgoing energy flux density \(J_{out}\) consists of two contributions: thermal conduction \(J_{th}\) by the gas and radiation cooling \(J_{rad}\). In the pressure range considered here the thermal conduction is governed by the Knudsen theory [101, 120]:

\[
J_{th} = \frac{c_p}{c_v} + \frac{1}{16(c_p/c_v - 1)} \frac{p}{T_g} \sqrt{\frac{k_b}{\pi m}} \alpha(T_p - T_g),
\]

where \(c_p/c_v = \gamma\) is the heat capacity ratio (adiabatic coefficient), \(m\) is the gas molecule mass, \(p\) is the gas pressure, \(k_b\) is the Boltzmann constant and \(\alpha\) is the accommodation coefficient. The accommodation coefficient accounts for the fact that the desorbing gas atoms or molecules are not necessarily in equilibrium.

The radiation cooling term \(J_{rad}\) follows directly from the Stefan-Boltzmann law:

\[
J_{rad} = \varepsilon \sigma (T_p^4 - T_g^4),
\]
where $\varepsilon$ denotes the emissivity, and $\sigma$ is the Stefan-Boltzmann constant ($\sigma=5.67\times10^{-8}$ Wm$^{-2}$K$^{-4}$).

### 7.5.2 Argon plasma

In the stationary case where the particles are heated to their equilibrium temperature $T_p$ the energy fluxes are equal: $J_{in} = J_{out}$. Hence, by knowledge of the outgoing flux $J_{out}$ that consists of the thermal conduction $J_{th}$ and the radiation $J_{rad}$ the total energy flux towards a powder particle can be obtained and compared with model calculations.

![Figure 7.22: Results of the temperature measurements of MF dust particles trapped in a 20 Pa argon plasma, as a function of RF power.](image)

In accordance with Eqs. (7.25) and (7.26) the loss terms are essentially determined by the particle temperature $T_p$ and the gas temperature $T_g$ which have been measured, see Figs. 7.8 and 7.22. Note that the difference between particle temperature and gas temperature is almost constant. For argon the adiabatic coefficient is $\gamma=5/3$ and the accommodation coefficient $\alpha=0.86$ has been suggested in literature [117]. The emissivity of the polymer-like MF particles is supposed to be 0.9 [121]. By using these values the energy losses by gas cooling and heat radiation of a particle suspended in an argon rf plasma are calculated. The results are shown in Fig. 7.23. For the used pressure of 20 Pa the cooling by radiation is stronger than the cooling by the gas conduction. This observation is in agreement with other authors [122].
Figure 7.23: Energy losses of MF particles in an argon plasma of $p=20\text{Pa}$. The total loss consists of the contribution by radiation and gas conduction.

Figure 7.24: The different components of the energy influx for an argon plasma consisting of $J_e$, $J_i$, and $J_{rec}$. 
In Fig. 7.24 the calculated components (Eq. 7.18) for the energy influx are depicted: the energy influx consists of \( J_e, J_i, \) and \( J_{rec} \). In the case of an argon plasma only the energetic contributions due to kinetic energy of the charge carriers (Eqs. 7.19 and 7.20) and their recombination (Eq. 7.22) have to be considered; the recombination clearly dominates the energy influx. Because of the inert gas behavior the contributions due to molecule association and chemical reactions with the particle surface can be neglected. In order to calculate \( J_e, J_i, \) and \( J_{rec} \) the internal plasma parameters obtained by Langmuir probe measurements (see Figs. 7.18, 7.19, and 7.20) and/or typical literature values for a GEC cell under comparable experimental conditions [123 - 125], respectively, have been taken.

In Fig. 7.25 the energy influx \( J_{in} \) has been compared with the determined energy outflux \( J_{out} \) based on the temperature measurements. As it can be seen in Fig. 7.25 the calculated energy influx is in a quite good agreement with the measured values of \( J_{out} \). Since the MF particles are at floating potential the heating by kinetic energy of the \( \text{Ar}^+ \) ions and electrons is small due to the rather small potential drop between plasma and floating potential. The dominant contribution is the recombination of the charge carriers.

Apparently the assumptions that the accommodation coefficient equals \( \alpha = 0.86 \), and that the emissivity of the MF particle equals 0.9 are justified. Furthermore, the results indicate that a description of the energy influx by charge carriers, which are characterized by plasma diagnostics, is an appropriate tool for the treatment of plasma-particle interaction. On the other hand the use of micro-particles as thermal probes in an argon plasma has been successfully demonstrated.

### 7.5.3 Oxygen plasma

During oxygen plasma treatment of the hydrocarbon/nitrogen-containing MF particles (\( \text{C}_3\text{H}_6\text{N}_6 \) and \( \text{CH}_3\text{O} \) highly cross-linked molecule) the energy fluxes towards the substrates...
have been determined by measurements of $T_p$ in the same way as for argon. However, now the contributions to the total energy influx in addition to the kinetic ion energy transfer are also due to recombination of atomic species (association) and exothermic combustion reactions of the plastic-like particles by the plasma generated oxygen radicals [56, 67]. Etching of the particles confirms the chemical reaction process that may be attributed to the following mechanisms:

- Chemical surface film reactions (SFR) of the particle surface layers with oxygen atoms which are produced in the collision dominated sheath region and in the negative glow by dissociation of O$_2$ molecules, and
- Chemical sputtering (CSP) by energetic O$_2^+$- and O$^+$-species colliding with the particles.

However, the latter as well as Physical sputtering (PSP) of the particle surface are less important. Since the particles are at floating potential, the energy for efficient sputtering is too low. Otherwise, also in the inert argon plasma, particle etching would be observed. But even for very long process times ($t > 30 \text{ min}$) in this case the particle size was constant as measured by Mie scattering ellipsometry and angular resolved forward scattering. Hence, plasma etching of confined MF particles will proceed only by the chemically reactive oxygen radicals and ions.

![Figure 7.26](image)

**Figure 7.26:** The results of the temperature measurements, performed on a cloud of RhB-doped MF particles immersed in a 20 Pa oxygen plasma as a function of RF power.

By using the measured particle temperature $T_p$ (see Fig. 7.26) the energy loss has been estimated again according to Eqs. (7.25) and (7.26). For oxygen in Eq. (7.25) the adiabatic coefficient is $c_p/c_V = 7/5$ and the accomodation coefficient has been taken in accordance to [126] as $\alpha = 0.9$. During etching the emissivity of the particle does not change, therefore it remains $\varepsilon = 0.9$ in Eq. (7.26). The results for the particles energy loss $J_{out}$ in an oxygen
plasma as a function of power is shown in Fig. 7.27. Similarly to the argon plasma, for low pressures \( p = 20 \text{ Pa} \) the cooling by radiation is dominant, too.

As described above, the loss has to be balanced by the incoming contributions with regard to particle heating due to charge carriers and radical association and chemical reaction. The particle density \( n_O \) of the oxygen atoms is mainly determined by electron impact processes taking place in the glow region:

\[
\begin{align*}
O_2 + e_f &\rightarrow O_2^+ + 2e \\
O_2^+ + e_f &\rightarrow O^+ + O + 2e \\
O_2 + e_f &\rightarrow O + O + e.
\end{align*}
\]

The abbreviation \( e_f \) stands for fast beam electrons released by secondary electron emission at the cathode (\( \gamma \)-process) [115]. The low energy plasma electrons \( (e_l) \) which exist in the glow in a rather high density generate preferably negative molecule ions by electron attachment. However, they decay into more stable negative atom ions and oxygen atoms, respectively:

\[
\begin{align*}
O_2 + e_l &\rightarrow O_2^-
\end{align*}
\]

\[
\begin{align*}
O_2^- &\rightarrow O^- + O \\
O_2^- &\rightarrow O + O + e.
\end{align*}
\]

The preferred generation of negative ions also contributes to the formation of oxygen atoms by charge exchange:

\[
\begin{align*}
O^- + O_2 &\rightarrow O + O_2^- \\
O^- + O_2 &\rightarrow O^+ + O_2 + 2e.
\end{align*}
\]

The efficiency of oxygen ionization and dissociation depends on the electron energy distribution function (EEDF) and the electron density. Both are strongly influenced by the power and gas pressure in the discharge. Unfortunately, there are only complete data sets of the plasma parameters available for high power. The dissociation degree which is in the order of 0.01 ... 0.05 under our experimental conditions results in values for \( n_O \) of about \( 2 \times 10^{20} \text{ cm}^3 \) [127]. The other quantities which are necessary to calculate the contribution \( J_{\text{ass}} \) in Eq. (7.26) are: \( E_{\text{diss}} = 5 \text{ eV} \) and \( \Gamma_O = 0.12 \). Under these assumptions, the contribution of oxygen radical association to the total heat flux is in the order of 5% as indicated in Fig. 7.28.
Figure 7.27: Energy losses of MF particles in an oxygen plasma of $p=20$ Pa. The total loss consists of the contribution by radiation and gas conduction.

Figure 7.28: Comparison of the calculated energy influx for an oxygen plasma $J_{in}$ consisting of $J_e$, $J_i$, $J_{rec}$, $J_{ass}$, and $J_{chem}$ with the measured energy loss $J_{out}$ as determined in Fig. 7.28.

The rather high inflow of oxygen atoms towards the substrate leads also to reactions with the MF particles surface. The surface density of atoms of the MF particles is in the order of $10^{14}...10^{15}$ cm$^{-2}$. Thus, the relatively high particle influx results in surface reactions...
with oxygen even if the sticking probability of the reactive atoms at the MF surface should be small. The removal (etching) of the products is influenced by the thermal conditions at the surface.

The used MF particles are polymerized \( \text{C}_3\text{H}_6\text{N}_6 \) molecules. The combustion heat of this material is \( 2.16 \times 10^4 \text{ kJ/kg} \) [128] and the heat released by combustion has been determined according to Eq. (7.24) to be in the order of 5% that is comparable to the contribution by association, see Fig. 7.28.

However, again as in the case of an argon plasma the recombination of positive ions, electrons, and possibly negative ions, is again the dominating part in the energy balance of an particle confined in an oxygen plasma.

### 7.6 Conclusions

We have demonstrated that in-situ laser induced fluorescence of dyed dust particles allows for a determination of the internal particle temperature. If these measurements are combined with measurements of the electron density, electron temperature, gas temperature and particle etch rate, all input parameters of the thermal balance of the particles are known. The dominant heating mechanisms for argon plasmas are particle heating due to charge carrier recombination. For oxygen plasmas also a small contribution due to radical recombination of oxygen atoms to molecules is important. Both loss mechanisms, heat conduction and radiation cooling, are of equal importance. The calculated influx and outflux agree quite well.

In short, the in-situ thermometry method introduced in this chapter actually turns the suspended particles into microprobes for the particle energy balance, and indirectly also to microprobes for the balance between the several plasma-surface interaction mechanisms.
8. References


References


[128] H. Wulff, Department of Chemistry, University of Greifswald, Thanks are due to H. Wulff who calculated the combustion heat of MF on the basis of a code.
Summary

In the last decade, the formation of dust particles in processing plasmas has received a lot of attention. In those environments, dust formation often is unwanted: it can e.g. reduce production yield or deteriorate film quality. The discovery of the Coulomb crystal, which is an analogy for a solid state crystal, shows that dust formation also has its benefits. Also the perspective to the production of particles with unique and desired qualities for e.g. ceramics, catalysis, and optoelectronics is attractive. In order to gain information about the dust particles in these three fields, it is necessary to use suitable diagnostics, which are capable of monitoring small changes inflicted on the particles.

In this thesis optical studies of micrometer-sized dust particles immersed in radio-frequency plasmas are described. The dust particles are injected into the plasma, where they acquire a net negative charge. This charge prevents the particles to escape from the plasma. When the right conditions are chosen, it is possible to confine the particles to a stable position for a long time. In this situation, optical techniques can be applied to measure the influence of the radio-frequency (RF) plasma on the particles.

Two of these techniques, rotating compensator ellipsometry (RCE) and Mueller matrix ellipsometry (MME) are based on the same method: the ellipsometric analysis of the change of the polarization state of the scattered light induced by the dust particles. The main difference between the two methods is the number of rotating components; the RCE has one rotating component and analyses a part of the matrix describing the polarization behavior of the dust particles. The MME has two rotating components and measures the full matrix. Both diagnostics measure the scattered light at an angle of 90° in the horizontal plane with respect to the undeflected beam. With the two techniques the etching of the polymer particles in oxygen RF plasmas has been monitored. In both situations the size of the particles decreases as a result of the plasma operation. From the RCE measurements it can be inferred that the width of the particle size distribution increases. The MME measurements are performed on single particles and point out that the particles remain spherical during their treatment.

A third technique is used to measure the angle resolved scattering profile of single particles in the forward direction. One single particle is injected in the plasma and illuminated with a vertically polarized laser beam. The scattering, which is described by the well-known Mie theory, is recorded in the forward direction in the horizontal scattering plane. This method allows for a very accurate determination of particle size and refractive index. It takes time to record the angular profile, and as a consequence the plasma can cause the particle size to change during the measurement. This is beneficial, as it now becomes possible to determine, in addition to the particle size and the refractive index, the etch rate of the particle from one single angular resolved profile.

In this thesis also a fourth optical technique is applied to the particles. In contrast to the other three diagnostics, now the particle has been used to study the plasma. In the plasma a cloud of dyed dust particles is injected. The dye, Rhodamine B, has been shown to emit a temperature-dependent fluorescent emission spectrum. In the plasma, the particles are illuminated with an argon ion laser and subsequently the resulting fluorescent emission is recorded. The fluorescent emission depends on the plasma parameters. The particle temperature increases with increasing RF power. These measurements are combined with high-resolution atomic absorption spectroscopy measurements that give information on the gas temperature. Furthermore, Langmuir probe measurements have
been performed which yield the electron density and temperature, the ion density, the floating potential, and the plasma potential. All these data have been used to determine the particle thermal balance, i.e. the fluxes arriving at and leaving from the particle. A good agreement has been found between experiment and theory: the dust particles can be used as microprobes.
Samenvatting

In het laatste decennium heeft de vorming van poederdeeltjes in plasma's voor oppervlaktemodificatie veel aandacht gekregen. In die omgeving is stofvorming vaak ongewenst: het leidt bijvoorbeeld tot een productieafname of een verslechtering van de laagkwaliteit. De ontdekking van het zogenaamde Coulombkristal, dat een analogon is voor een vaste stofkristal, heeft getoond dat stofvorming ook haar positieve kanten heeft. Ook het vooruitzicht van de productie van poeders met unieke en gewenste eigenschappen, denk bijvoorbeeld aan keramische, katalytische of opto-elektronische toepassingen, is aantrekkelijk. Om kennis te vergaren betreffende de poeders in elk van de drie toepassingsgebieden, is het noodzakelijk om over geschikte diagnostieken te kunnen beschikken hebben die het vermogen hebben om kleine veranderingen van de poederdeeltjes te kunnen waarnemen.

In dit proefschrift wordt optisch onderzoek aan micrometer-grote poederdeeltjes beschreven. Die poederdeeltjes zijn opgesloten in radiofrequente plasma's. Ze worden in het plasma geïnjecteerd, waar zij een netto negatieve lading verzamelen. Deze lading verijdelt de ontsnapping van de deeltjes uit het plasma. Indien de goede condities gekozen worden, dan is het mogelijk de poeders gedurende een lange tijd te fixeren. In deze situatie is het mogelijk om met behulp van optische technieken de invloed van het radiofrequente plasma op de deeltjes te bestuderen.

Twee van deze technieken, roterende compensator ellipsometrie (RCE) en Mueller matrix ellipsometrie (MME) zijn gebaseerd op dezelfde methode: de ellipsometrische analyse van de verandering van de polarisatietoestand van het verstrooide licht, die wordt geïnduceerd door de poederdeeltjes. Het belangrijkste verschil tussen de twee methodes is het aantal roterende componenten: de RCE heeft één roterende component en analyseert slechts een gedeelte van de matrix die het polarisatie-gedrag van de poederdeeltjes beschrijft. De MME heeft twee roterende componenten en meet de gehele matrix. Beide diagnostieken meten het verstrooide licht in het horizontale vlak onder een hoek van 90° opzich van de onverstoorde bundel. Met beide technieken wordt het etsen van polymeerdeeltjes in radiofrequente plasma's bekken. Uit de RCE-metingen kan geconcludeerd worden dat de breedte van de deeltjesgrootteverdeling toeneemt. De MME-metingen zijn verricht aan individuele deeltjes en geven aan dat de deeltjes bolvormig blijven gedurende hun behandeling.

Een derde techniek wordt gebruikt om het verstrooingsprofiel van een individueel deeltje hoekopgelost te meten in de voorwaartse richting. Eén enkel deeltje wordt daartoe in het plasma geïnjecteerd en belicht met een vertikaal gepolariseerde laserbundel. De verstrooing, beschreven met behulp van de bekende Mie theorie, wordt in het horizontale vlak gemeten in de voorwaartse richting. Deze methode maakt een nauwkeurige bepaling van deeltjesgrootte en brekingsindex mogelijk. Het kost tijd om een hoekopgelost profiel te meten en dit heeft de consequentie dat onder invloed van het plasma de poederdeeltjes kan veranderen. Dit is gunstig omdat het nu mogelijk wordt om zowel de deeltjesgrootte en brekingsindex als de etssnelheid van het poederdeeltje te bepalen uit één enkel hoekopgelost profiel.

In dit proefschrift is nog een vierde diagnostiek toegepast op de deeltjes. In tegenstelling tot de drie andere diagnostieken, wordt nu het poederdeeltje gebruikt om aan het plasma te meten. Een wolk van poederdeeltjes, behandeld met kleurstof, wordt in het plasma geïnjecteerd. Het is aangetoond dat de kleurstof, Rhodamine B, een temperatuurafhankelijk fluorescentiespectrum uitzendt. In het plasma, worden de deeltjes belicht met een argon-ion laser en vervolgens wordt het fluorescentiespectrum
Dankwoord

Ik wil graag de volgende mensen bedanken die allemaal op hun eigen manier hebben bijgedragen aan de totstandkoming van dit proefschrift.

Eerste promotor Frits de Hoog en copromotor Gerrit Kroesen voor de begeleiding de afgelopen vier jaar.

Hans Deutsch and Holger Kersten for the good time I had in Greifswald (too short!).


De studenten: Wout de Zeeuw, Niek Simons, Marjorie Moreau, Philippe Mazet, Mohamed Boufnichel, Rob Puts en Daan Damen.

De medewerkers van de werkplaats en met name Marius Bogers.

Eric Timmermans en Richard Engeln voor hun hulp bij de absorptiemetingen. Ook alle andere collega’s van de groep ETP.

Hubertus Thomas, Uwe Konopka and Milenko Zuzic for the pleasant period at the DLR.

En mijn vrienden, mijn ouders, Noor, Mariëlle en Marieke voor hun steun.

Curriculum Vitae

16 juli 1970 geboren te Eindhoven

1982 - 1987 HAVO, Van der Puttlyceum, Eindhoven

1987 - 1989 Atheneum, Van der Puttlyceum, Eindhoven

1989 - 1995 Technische Natuurkunde, Technische Universiteit Eindhoven

1995 – 1999 Promotieonderzoek in groep EPG, Faculteit Technische Natuurkunde, Technische Universiteit Eindhoven