

Theoretical and Experimental Studies Related to the Compositional and Microstructural Evolution of Alumina Thin Films

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Eva Johanna Lovisa Rosén

aus Habo, Schweden

Berichter: Univ.-Prof. Jochen M. Schneider, Ph. D.
Univ.-Prof. Dr.rer.nat. Matthias Wuttig

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Abstract

In this thesis, the correlation between plasma chemistry / ion energy and thin film composition / microstructure for cathodic arc deposited alumina thin films is investigated. To contribute towards understanding this correlation, both theoretical and experimental investigations have been performed. The plasma, constituting the feed-stock material for the film growth, was characterized with respect to chemistry, for a pulsed arc showing a temporal dependence from pulse-to-pulse as well as within a pulse. Further plasma analysis of a DC arc source showed charge- and pressure dependent ion energy distributions including ions in excess of 200 eV, which could be manipulated by suitable magnetic field configuration. Based on the here determined plasma composition data, thin film growth related theoretical studies have been carried out, using *ab initio* calculations and *ab initio* molecular dynamics simulations based on Density Functional Theory. The sequence of an ion approaching and being incorporated in the top surface layers was divided into separate investigations related to structural evolution; ion-surface interaction prior to adsorption, adsorption, surface migration and local structural changes induced by ion bombardment. The results may in part explain the experimentally observed formation of amorphous structures during kinetically limited alumina film growth. Furthermore, possible hydrogen incorporation in the film due to presence of residual gas motivated a study related to compositional evolution. The simulation results suggest that hydrogen desorption upon ion – surface interaction may be possible. To correlate theoretical studies and synthesis conditions with phase formation, experiments were performed to investigate the effect of ion energy and substrate temperature on the film composition and microstructure. It was found that the structure evolution strongly depends on the to the surface supplied energy, and that γ -alumina forms at temperatures as low as 200 °C. Analysis of the film composition showed a low concentration of impurities, with less than 0.25 at% hydrogen. Hence, the results presented in this thesis may provide pathways to crystalline film growth at low temperatures as well as to reduction of impurity incorporation during film growth.

Preface

The work presented in this thesis is a summary of research performed at RWTH Aachen University (Materials Chemistry group), Uppsala University (Materials Chemistry group), and Linköping University (Thin Film Physics Division). Close collaboration has also been conducted with the Plasma Applications Group at Berkeley National Laboratory.

Publications

Papers contributing to the thesis

- Paper I** **Plasma chemistry fluctuations an a reactive arc plasma in the presence of magnetic fields**
J. Rosén, A. Anders, and J. M. Schneider
Appl. Phys. Lett. **80**, 4109 (2002)
- Paper II** **Temporal development of the composition of Zr and Cr cathodic arc plasma streams in a N₂ environment**
J. Rosén, A. Anders, L. Hultman, and J. M. Schneider
J. Appl. Phys. **94**, 1414 (2003)
- Paper III** **Charge state and time resolved plasma composition of a pulsed zirconium arc in a nitrogen environment**
J. Rosén, A. Anders, L. Hultman, and J. M. Schneider
J. Appl. Phys. **96**, 4793 (2004)
- Paper IV** **Thin film growth related adsorption study of Al and O ions on an α -Al₂O₃ surface**
J. Rosén, J. M. Schneider, and K. Larsson
Accepted for publication in J. Phys. Chem. B
- Paper V** **Effect of ion energy on structure and composition of cathodic arc deposited alumina thin films**
J. Rosén, S. Mráz, Ulrich Kreissig, D. Music, and J. M. Schneider
Accepted for publication in Plasma Chem. Plasma Proc.
- Paper VI** ***Ab initio* Molecular Dynamics study of ion surface interactions**
J. Rosén, J. M. Schneider, and K. Larsson
Accepted for publication in Solid State Commun.

- Paper VII** ***Ab initio* studies of adsorption and migration surface processes on an α -Al₂O₃ surface**
J. Rosén, J. M. Schneider, and K. Larsson
Submitted for publication
- Paper VIII** **Charge-state-resolved ion energy distributions of aluminum vacuum arcs**
J. Rosén, A. Anders, S. Mráz, and J. M. Schneider
Submitted for publication
- Paper IX** ***Ab initio* Molecular Dynamics study of hydrogen removal by ion-surface interactions**
J. Rosén, K. Larsson, and J. M. Schneider
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1. Introduction

This chapter provides a brief introduction to the research area. Furthermore, the motivation for the research as well as research aims are discussed.

An essential part of materials science is the study of properties of materials and how those properties are determined by composition and microstructure. To understand this relationship is of importance for tailoring material properties. Structure and composition in turn can be affected by the synthesis conditions employed, see Figure 1.1. A fundamental understanding of the process is beneficial, and research concerning the relationships between synthesis, structure, properties and performance enables synthesis of advanced materials.

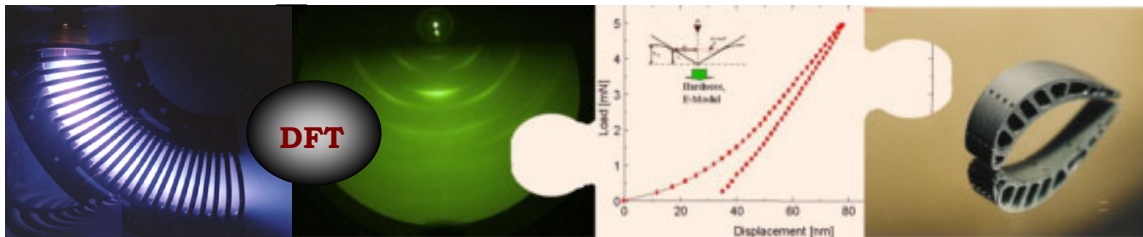


Figure 1.1 Materials science involves research on the correlation between synthesis, structure, properties and performance.

This work concerns the relation between synthesis, composition and microstructure of thin films, with specific model systems as presented below. To

begin with, some general concepts will therefore be introduced to provide a brief introduction to the research area.

Thin film growth is a process where a thin layer of material (coating) is deposited onto another material (substrate) in order to achieve properties that can not be attained by the substrate or coating material alone. Thin films may be produced by either chemical vapor deposition (CVD) or physical vapor deposition (PVD), where the source of the film forming material is gas and solid, respectively.[1] Sputtering and cathodic arc are examples of versatile PVD processes, both plasma based. A plasma is generally described as a partially ionized gas, consisting of atoms, electrons and ions. In sputtering, the vapor is formed by energetic particle bombardment of a target material, causing ejection of mainly atoms. Cathodic arc, on the other hand, can be described as micro explosions occurring on the cathode surface, resulting in a highly ionized plasma.[2] The high degree of ionization is advantageous, since the ion energy can easily be affected by electric fields.[3]

Major parameters affecting the microstructure evolution of thin films include the ion energy and the plasma chemistry. These parameters will be discussed below, followed by related questions that this work aims to answer.

A key feature of energetic ions impacting on a surface, is the energy transfer to the surface atoms, in form of kinetic or potential energy. This may result in enhanced ad-atom mobility compared to thermal condensation, which in turn affects the resulting film structure and film properties.[4] Figure 1.2 shows several examples of possible effects of ion bombardment on surface atoms.[5] Furthermore, it is well known that the ion energy affects the microstructure evolution during thin film growth, through for example the nucleation density and defect formation.[6]

In order to control the ion energy and to study its effect on the thin film growth, one needs to investigate and control the plasma chemistry including the charge state distribution. An approximate expression of the kinetic energy E_i of an ion i , reaching the substrate, can be written

$$E_i = E_0 + Qe\Delta U \quad (1.1)$$

where E_0 is the initial kinetic energy of the ion, Q is the ion charge state and e is the elementary charge. As the plasma travels towards the substrate surface, it is accelerated or decelerated due to the potential difference, ΔU , between the plasma and the substrate. Therefore, for a given initial energy and charge state, the ion energy can

be controlled by varying the substrate potential. The expression for the ion energy above shows the importance of degree of ionization and the charge state of the ions in the plasma.

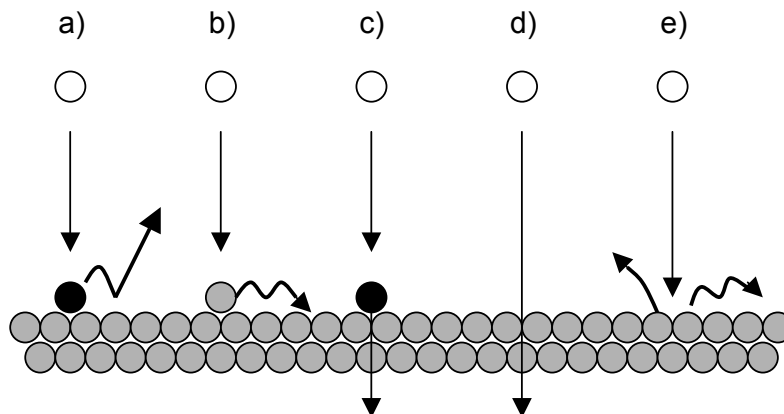


Figure 1.2 Effects of bombarding atoms on surface atoms: a) chemical activation or adsorbate removal, b) displacement, c) implantation of impurity or film atom, d) ion implantation, e) surface defect (vacancy) created by sputtering or displacement.[5]

Also crucial for the microstructure evolution is what different species are present. The finding of metal atoms/ions from the target/cathode material and gas ions from the intentionally introduced gas is expected. Additionally, there is also residual gas present. In a high vacuum growth chamber the gas contains mainly water, but for example nitrogen, oxygen and carbohydrates may also be present.[7] These contaminants result in the introduction of impurities in the film, which may be important with respect to film composition.

The main goal of this study is to investigate and contribute towards understanding the correlation between plasma chemistry / ion energy and film composition / microstructure. Since the plasma is the feed-stock material for the thin film growth process, characterization of arc plasma has been performed and reported in the literature, both in vacuum and in a reactive environment. However, most data presented have been collected as averages in a steady state regime of the plasma formation.

Very limited data is available describing the *temporal* development of the plasma chemistry and average charge state, which is of importance for the resulting compositional as well as structural evolution of the film.[6] One goal of this thesis is

to quantify this plasma chemistry-time dependence, and the question that therefore needs to be answered is:

- Is the plasma composition a function of time?

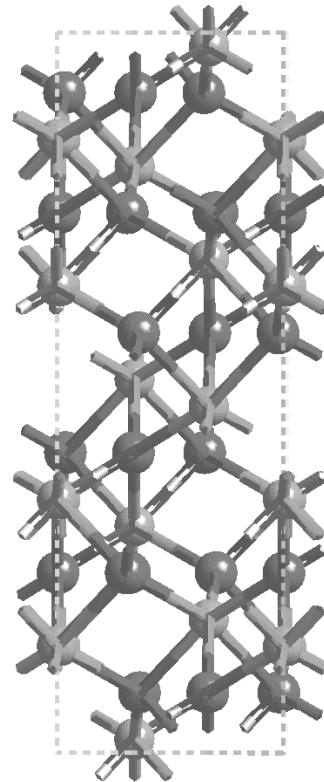
Therefore, the previously not reported pulse-to-pulse fluctuation of the plasma chemistry has been studied in the presence of magnetic fields. Furthermore, an investigation of time *and* charge state resolved plasma pulses has shown the plasma chemistry evolution *within* the pulse.

Limited data is available also for detailed description of the ion energy, E_0 . In addition to the vast material reported on averages, one should stress that the ion energies are *distributions*, where the shape and width may be decisive for film microstructure (previously not investigated). A part of this study is therefore an attempt to answer the questions:

- What is the form of the *charge state resolved* ion energy distributions in the arc plasma?
- ... and what ion acceleration mechanisms may cause these different distributions?

After a detailed plasma characterization, film growth has been performed by cathodic arc deposition. Alumina, Al_2O_3 , is the material investigated in the presented study. It is widely used due to its mechanical and physical properties, which are particularly suitable for electrical and thermal insulation,[8] wear-resistant [9] and diffusion barrier [10] coatings. The only thermodynamically stable phase is the α -phase, corundum, shown in Figure 1.3 with its rhombohedral crystal structure.

Figure 1.3 Unit cell of $\alpha\text{-Al}_2\text{O}_3$, side view. Darker spheres represent oxygen and brighter spheres aluminum.



Corundum has proved to be a challenge to attain during PVD processing at low temperatures, which is routinely obtained by thermal CVD at 1000 °C.[11] Amorphous structures are known to form at substrate temperatures ≤ 250 °C.[12] The transformation to the α -phase typically takes place close to 1000 °C,[13] where the transition sequence may include the γ -phase (cubic) and the θ -phase (cubic).[14]

Although there are many applications of the material, the fundamental understanding of it is not satisfactory. As a result there are publications showing diverging results of some of the material properties. An example is the large scattering in reported values of the elastic properties of amorphous alumina thin films, which recently was suggested to be in part due to hydrogen incorporation during film synthesis.[15]

The strategy to shed some light on the challenges that are associated with low temperature growth of alumina has been to carry out theoretical calculations, where the results of the plasma characterization presented in this thesis served as input parameters for the calculations. Also, based on these calculations, initial thin film growth experiments have been conducted. Overall, the investigations aimed to answer:

- How can the film microstructure be influenced?
- How can the film composition be influenced?

An attempt to answer the first question was made through film depositions of alumina with varying ion energy, combined with theoretical studies (Density Functional Theory). The latter gave atomic level information related to the film growth process: Ion-surface interaction prior to collision, ion / atom adsorption, surface diffusion and local structural changes accompanying surface bombardment. The last question mainly address the problem of unintentional incorporation of hydrogen in the films. Through plasma and film characterization combined with molecular dynamics simulations, the effect of ion energy on the hydrogen incorporation was investigated.

In summary, the objective of the here presented research is to contribute towards understanding the relationship between the growth process and structural and compositional evolution of thin alumina films.

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2. Cathodic arc

This chapter provides an introduction to the deposition technique investigated here. Particular attention is paid to the plasma generation, plasma evolution during expansion, and condensation. More information can be found in reviews by Anders [1] and Brown.[2,3]

2.1 Introduction to the arc technique

A cathodic arc can be described as a low-voltage high-current plasma discharge between two metallic electrodes, in vacuum or in a gas environment, see Figure 2.1.[4] The plasma necessary for the current transport between the electrodes is formed at discrete micron-sized sites, called cathode spots, at the cathode surface. The formation of these spots is related to the mechanism of electron emission, and the resulting spot plasma is characterized by current and plasma density in the range of $\leq 10^{12}$ A/m² and $\leq 10^{26}$ m⁻³, respectively.[5] The plasma pressure of a spot is consequently high, and the strong pressure gradient together with local electric fields cause the plasma to accelerate away from the cathode surface.[1]

Plasma production in the cathode spots is characterized by a high degree of ionization (up to 100% has been reported).[3] The presence of multiply charged ions with a kinetic energy in the range 20-160 eV is well documented.[6,7] It is reported that this is beneficial in terms of process control and coating quality that can be achieved.[8]

A potential drawback of the cathodic arc method is the formation of liquid droplets, so called macroparticles, which affect the quality of the coating in an undesirable way.[4] Efforts have been made to reduce or eliminate these particles, successfully with various forms of macroparticle filters.[9]

A cathodic arc is often operated in a reactive background gas, as for example to achieve the formation of compounds such as oxides or nitrides. For further details on the technique and mechanisms of the cathodic arc process, see references.[3,10-12]

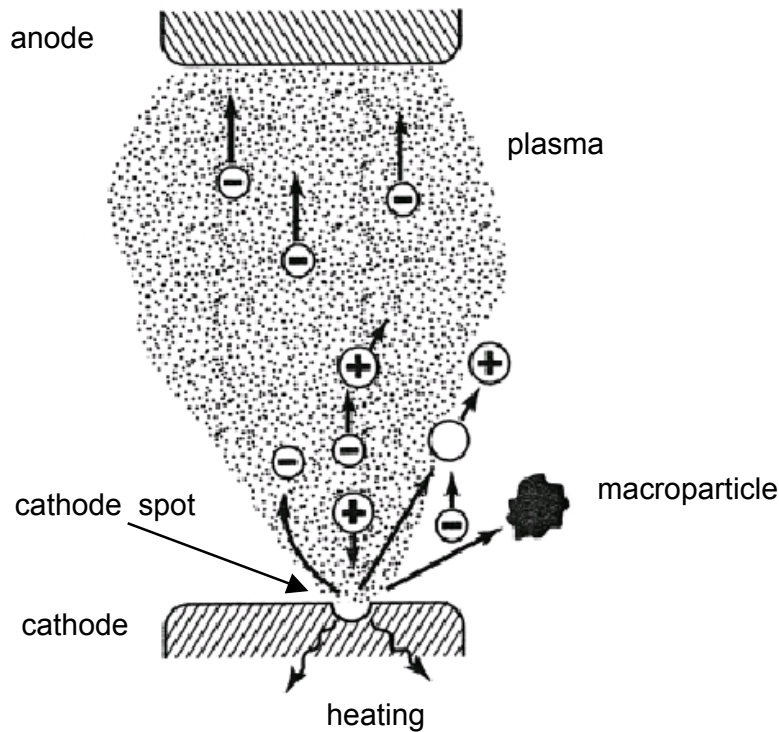


Figure 2.1 Plasma generation in a cathodic arc discharge.[4]

2.2 Plasma generation

The plasma originating from the cathode surface is strongly dependent on the surface state of the cathode. To initiate plasma production, electrons need to be emitted from the surface, and the roughness as well as the chemistry govern what electron emission mechanism is most probable. Examples include thermionic emission and field emission, which results in the formation of “plasma production

centers”, cathode spots, at the surface.[4] In the spot, the cathode material suffers a transition from the solid phase to a plasma phase, which expands away from the surface mainly due to a strong pressure gradient. There are several theories about cathode spot formation, see further details in references.[13,14]

One distinguishes between two different types of spots; those on surfaces which have reacted chemically to form a compound layer (type 1) and those on clean metal surfaces (type 2). Both the appearance and the properties of these two types differ; the tendency of type 1 is spot splitting, see Figure 2.2, and an increase in spot velocity as compared to type 2.[15,16]

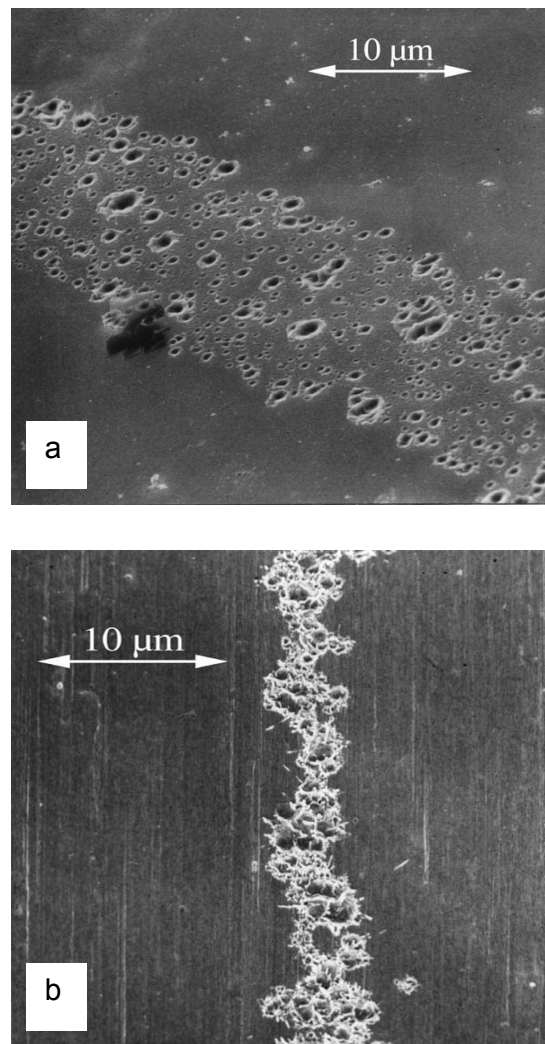


Figure 2.2 Figures courtesy of B. Jüttner, Berlin, Germany, showing a) spot type 1 (on a contaminated surface), and b) spot type 2 (on a clean surface).

Introducing reactive gas, such as for example N_2 or O_2 , may result in chemical reactions with the cathode material [17] and consequently the formation of spots of type 1 as the arc is ignited. As these spots move over the surface generating plasma, the compound layer formed is eroded, followed by a transition to spots of type 2 which “burn” in the bulk material.

Generally, the variety of cathodic arc production can be classified by plasma generation vs time. If the arc is sustained only for the duration of for example the discharge of a capacitor, it is designated “pulsed”, see Figure 2.3. Correspondingly, if the arc is sustained by a DC current source and uninterrupted, it is designated “continuous” (also referred to as DC arc). In these sources, there are several ways to initiate the plasma production; for example triggering through mechanical contact of an electrode, laser ablation, or high voltage flashover.[18,19] Below, the principles of the arc sources used in this work will be presented.

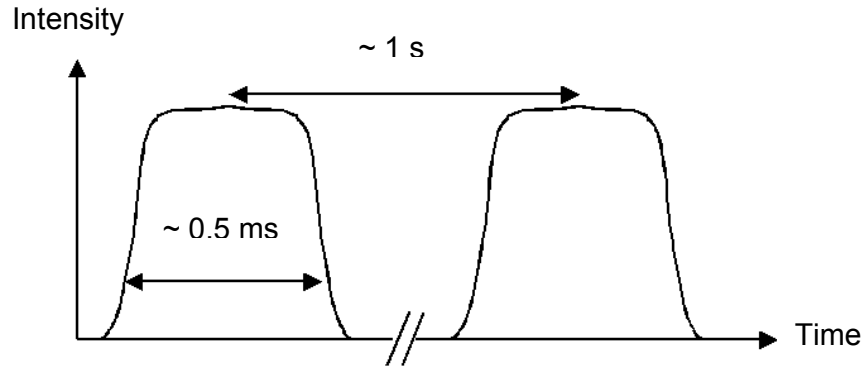


Figure 2.3 Schematic diagram of pulsed plasma generation.

2.2.1 Pulsed arc

There are several advantages of pulsed arc sources: For instance, the arc duration is typically short enough to not require cathode cooling, as well as to confine the arc spot to the cathode surface. Furthermore, the average power of the system can be regulated by arc duty cycle rather than the arc current.[20]

The triggering method used in the here presented investigations is “triggerless” arc initiation,[21] which is reliable if a conductive path between the cathode and the anode is provided. A graphite layer is used on the insulating surface

separating the cathode and the anode, and a surface flashover causes the initial formation of cathode spots, see Figure 2.4. The arc is established when the initial plasma bridges between the cathode and the anode, and is maintained as long as the circuit delivers a current greater than the “chopping” current, which is the critical minimum current associated with the minimum metal plasma production. Here, the actual plasma pulse is formed by discharging a capacitor bank, typically resulting in pulses of $\sim 300 \mu\text{s}$ at a pulse repetition rate of $\sim 1 \text{ Hz}$ and an arc current of 200-400 A.

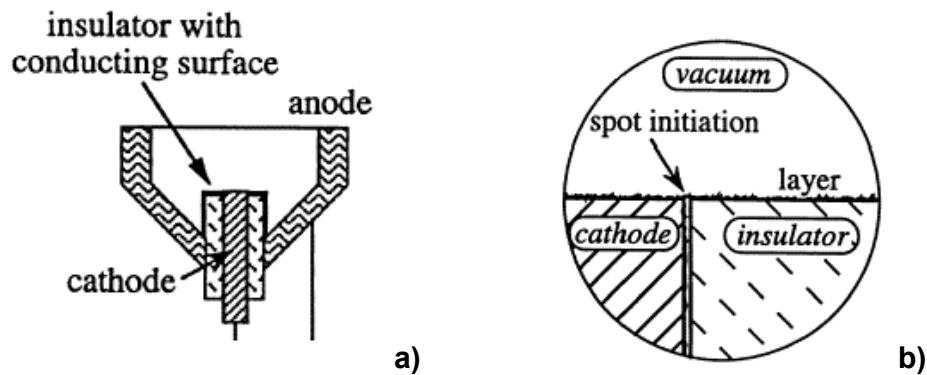


Figure 2.4 Cathode – anode configuration (a) and principle for “triggerless” arc initiation (b).[21]

2.2.2 Direct current (DC) arc

The low duty cycle of a pulsed arc source results in a low deposition rate. A continuous arc source have correspondingly higher deposition rate, but in most cases the cathode must be designed to dissipate the heat generated by the arc. Figure 2.5 shows schematically the source used in this work, both cathode and anode being cooled. The arc is ignited with the “triggerless” method as described above, resulting in continuous plasma formation sustained by a DC power supply. The cathode spots are confined to the cathode surface by a ring magnet located behind the cathode. Typical arc current used was 30-35 A.

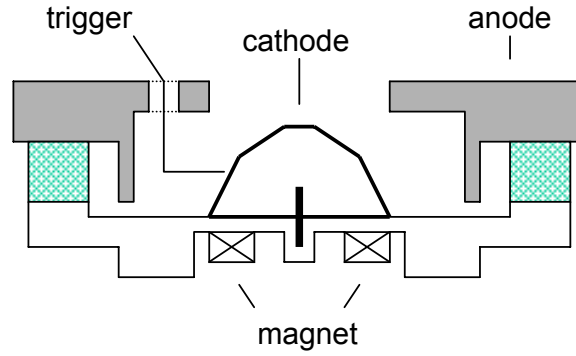


Figure 2.5 Cathode – anode configuration in the DC arc plasma source.

2.3 Plasma evolution during transport

Many attempts have been made to describe the plasma generation region and the plasma jet expansion. Here, a brief survey of common concepts, used to interpret our data, will be presented. Plasma evolution vs geometry will be discussed, divided in regions as schematically shown in Figure 2.6.

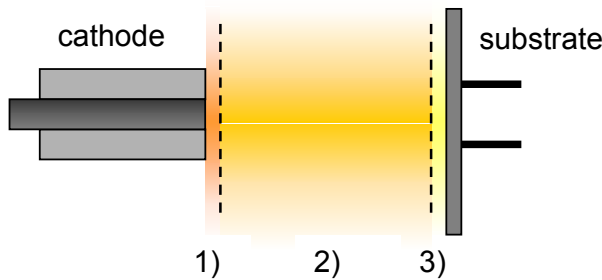


Figure 2.6 The plasma evolution discussion is divided in three regions; 1 (close to the cathode), 2 (in the plasma column) and 3 (close to the substrate).

2.3.1 Plasma evolution close to the cathode surface

The plasma density of the cathode spot ($\sim 10^{26} \text{ m}^{-3}$ [5]) results in near surface collisions, which is the reason why several models introduce a so called Knudsen layer.[22-24] It is a region within a few mean free paths of the cathode surface in which the velocity (energy) distribution function approaches equilibrium: The half-Maxwellian distribution (positive velocity v_x , cathode temperature) at the cathode

surface, is within the Knudsen layer changed into a shifted full Maxwellian in a center-of-mass coordinate system. The distribution function (converted into energy) can be written

$$f(E) = C \cdot E \cdot \exp\left[\frac{(\sqrt{E} - \sqrt{E_{cm}})^2}{T}\right] \quad (2.1)$$

where C is a constant and E , E_{cm} and T are the energy, center-of-mass energy, and temperature, respectively, in units of eV. After the Knudsen layer, further collisions may facilitate charge transfer reactions as well as ion acceleration, and hence changes of the distribution functions.

As previously mentioned, the arc plasma is highly ionized and contains multiply charged ions. All these ions together form the charge state distribution (CSD) of the plasma, which is strongly dependent on the cathode material and process parameters used. Attempts have been made to calculate the CSD near the cathode for vacuum arc plasmas,[25] using the Saha-equations:

$$\frac{n_e n_{Q+1}}{n_Q} = \Lambda_B^{-3} \frac{2 \sum_{Q+1}(T)}{\sum_Q(T)} \cdot \exp\left[-\frac{E_Q - \Delta E_Q}{kT}\right] \quad Q = 0, 1, \dots, Q_{\max} \quad (2.2)$$

n_e and N_Q are the densities of free electrons and ions of charge state Q , respectively, $\sum_Q$ is the partition function of the same ions, Λ_B is the thermal de Broglie wavelength, and $E_Q - \Delta E_Q$ is the ionization energy of the Q -fold charged ion with a correction due to particle interaction. These equations can be used under the assumption that the plasma is in thermodynamical equilibrium, and the ratios between the fractions of the differently charged particles are time-independent. The plasma is then said to be in Saha equilibrium (SE). That is the case close to the cathode spot where the plasma density is high enough for the rate of ionization and recombination to be considered equal.

As the plasma expands, the density and temperature decrease, and consequently also the frequency of ionizing and recombining collisions. At some point, a temperature and density dependent transition from Saha equilibrium (close to the spot) to non-equilibrium (far from the spot) occurs, as indicated by the red border in Figure 2.7. There the plasma “freezes”, in other words the chemistry and charge state ratios remain practically constant during the rest of the expansion. In the simplest model the transition is assumed to be instantaneous, see Figure 2.7a.

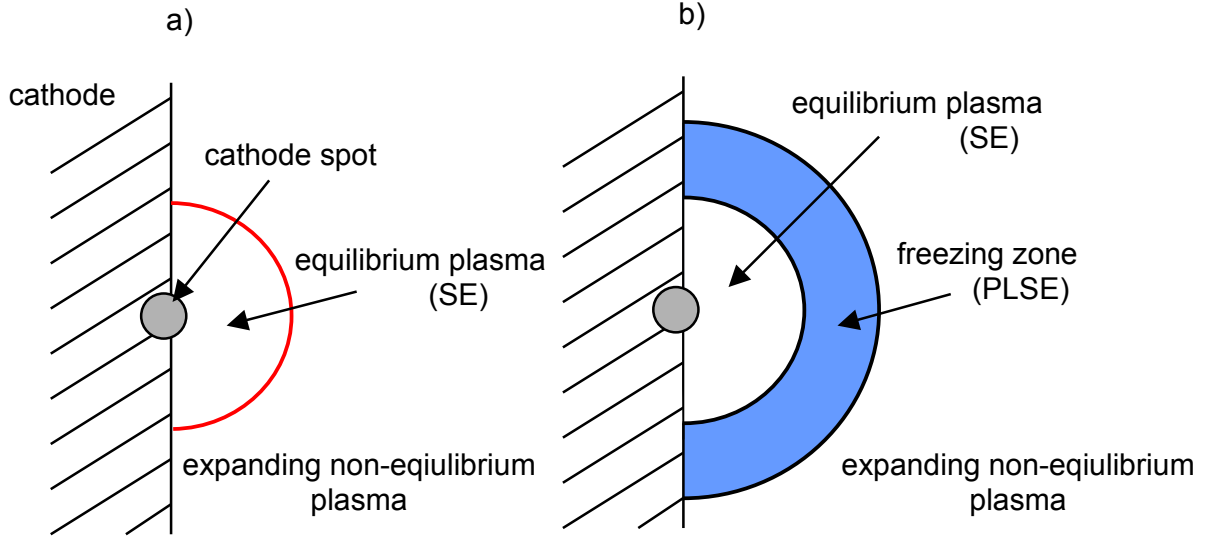


Figure 2.7 Expanding plasma, from equilibrium in the spot to non-equilibrium far from the spot. a) Instantaneous plasma freezing (infinitesimal transition zone). b) Successive plasma freezing (extended transition zone).

For several cathode materials, this approximation does not describe the measured values of the CSD.[25] Therefore, as an extended version, the model of partial local Saha equilibrium (PLSE) has been developed.[26] In this model the border is expanded into a transition zone, marked with blue in Figure 2.7b, and the freezing of the plasma takes place by successive freezing of the different charge states. Through studies of the ionization - recombination balance equations, it has been realized that the ions of highest charge will leave Saha equilibrium first, the remaining system being in PLSE.[26] Consequently, with decreasing temperature and density in the transition zone the remaining charge states will one after the other (according to their charge state magnitude) drop out of PLSE, until freezing is completed.

In order to also discuss the energy of these particles, we need to introduce a new concept, the burning voltage, which it is the potential difference between the cathode and the anode, as resulting from the schematic voltage profile in Figure 2.8.

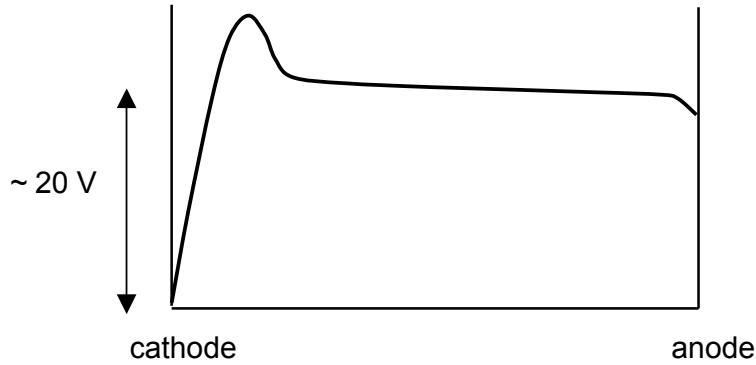


Figure 2.8 Approximate voltage profile in a vacuum arc, between a grounded cathode and the anode.

Almost all of the burning voltage drops in a very narrow region close to the cathode surface, called the cathode fall.[27] Therefore, the power P available for processes at the cathode spot can be written

$$P = U \cdot I \quad (2.3)$$

where U is the burning voltage and I is the arc current. U is cathode material dependent and can be of differently fluctuating character, which consequently affects the power, and in turn both the CSD and ion energy distribution (IED).[28]

Many theories have been suggested to account for ion acceleration mechanisms. The two most referred to is the potential hump theory [29] and the gasdynamic model.[30] The former predicts acceleration due to the potential difference caused by the electric field (see voltage profile with potential hump in Figure 2.8), and the latter states that electron-ion friction and expansion cooling (pressure gradient) are the main mechanisms responsible. Adjustments to these models have been made, see for example Refs. 31-32, which together with further investigations [7,33] suggest that the acceleration is based on pressure gradient coupled with electron-ion friction.

2.3.2 Plasma evolution in the plasma column

The plasma generation and evolution in a cathodic arc process can be divided in two parts; the forming and interaction at and in the immediate vicinity of the cathode surface (see Chapter 2.3.1), and the interaction and further development as the plasma expands out in the chamber. Of vital importance when discussing the plasma chemistry, charge state distribution (CSD), ion energy (IED) and changes thereof, is the presence of a (reactive) gas and / or a magnetic field.

As mentioned earlier, one of the drawbacks of the cathodic arc process is the formation of macroparticles. To reduce the macroparticle density, magnetic fields are often used to filter the plasma,[34] see Figure 2.9. Ions follow the electron trajectory which is defined by the magnetic field arrangement. Since the expansion direction of the neutrals and the macroparticles is unaffected by the magnetic field, macroparticle filtering is possible.

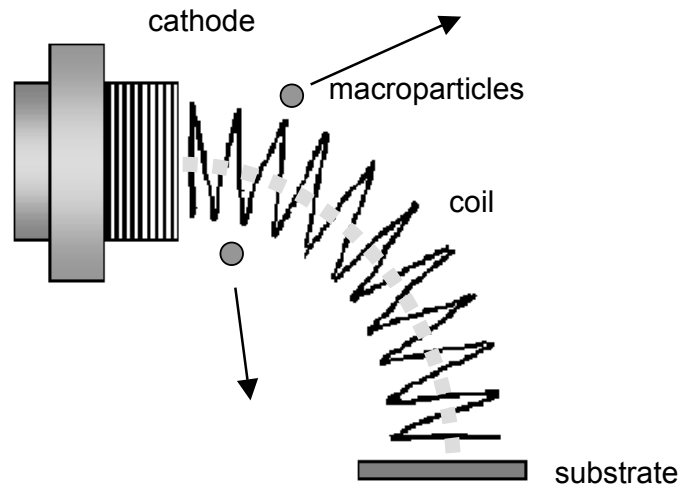


Figure 2.9 Macroparticle filtering of the plasma, using a curved coil.

When a magnetic field is applied, the electrons in the plasma are trapped and gyrate around the magnetic field lines. Therefore, their path length and residence time in the plasma volume of interest during expansion are increased. This results in a higher probability of electron impact ionization. Indications of this are shown both in terms of an increasing average charge state of the metal ions, and an increased concentration of non-metal ionic species.[35] These non-metal ions stem from

residual gas and/or intentionally introduced gas, and the concentration increases as the magnetic field strength increases.[36,37]

Compound thin films can be synthesized in the presence of a reactive gas. Apart from chemical reactions at the cathode surface, the gas also affects the expanding plasma. As the pressure increases, the probability of collisions between the metal ions and the gas molecules increases. A result of this is a more random expansion direction of the ions that have suffered from collisions, and therefore a reduced ion flux to the substrate. Another possible consequence of collisions is that charge exchange collisions may occur.[38] Energetically favorable reactions can then take place, resulting in a higher concentration of ions with lower charge at the expense of ions with higher charge. Besides an increased concentration of non-metal ions, a decrease in the average charge state is therefore also observed.[39]

2.4 Plasma at the substrate

When the plasma reaches the substrate region, the kinetic energy and charge can be described by energy distribution functions. A final “correction” to the energy of an ion can be made through applying a substrate bias potential (V_s), resulting in an increase or a decrease of the kinetic energy. Apart from perturbations at for instance a substrate, the plasma is virtually electric field free, and therefore equipotential. A term often used for this potential is the plasma potential (V_p). The kinetic energy of the ions and electrons in the plasma is therefore unaffected as the plasma expands towards the substrate (in the collision free case). If a potential is applied to the substrate, the difference between plasma and the substrate potential results in a potential energy hill for the ions and electrons arriving there. If the substrate potential is less than the plasma potential the positive ions will travel downhill in potential energy and gain kinetic energy, as seen in Figure 2.10. The electrons experience the opposite.

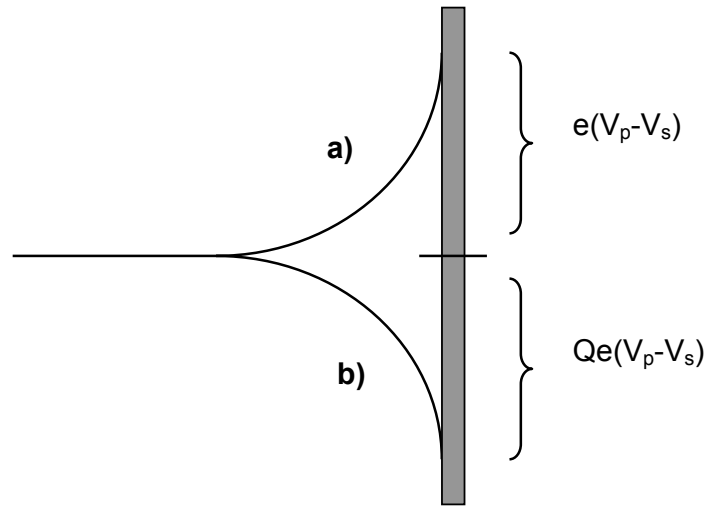


Figure 2.10 Variations of potential energy of a) an electron b) a positive ion with charge Q , in the vicinity of a negatively biased substrate.

Apart from the ion energy, the deposition of the film onto the substrate is influenced also by other deposition conditions. Examples of factors affecting the result are the substrate surface condition (including temperature) and the reactivity of the arriving plasma.[27]

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3. Plasma characterization

Here, the methods used to characterize the arc plasma are presented, followed by results of various investigations related to plasma chemistry and ion energy.

3.1 Techniques

The methods used to characterize the plasma were chosen according to our interest in both plasma chemistry and ion energy. A time-of-flight charge-to-mass spectrometer [1] and a mass-energy analyzer [2] were used for analysis of the pulsed and DC arc plasma, respectively.

3.1.1 Time-of-flight charge-to-mass spectrometer

To analyze the plasma chemistry of the pulsed arc discharge, a time-of-flight charge-to-mass spectrometer was used, described in detail in Ref. 1, and schematically shown in Figure 3.1. Ions of mass m and charge state Q are extracted from the ion source through a voltage drop V_{ext} , and gain a kinetic energy proportional to the charge state:

$$Q \cdot V_{ext} = \frac{mv^2}{2} \quad (3.1)$$

A 200 ns sample of the plasma beam formed is selected by gating plates, and drifts the distance L to the detector, a Faraday cup, measuring the ion current. The time-of-flight t of an ion is given by

$$\left. \begin{aligned} t &= \frac{L}{v} \\ v &= \sqrt{\frac{2 \cdot Q \cdot V_{ext}}{m}} \end{aligned} \right\} \Rightarrow t = \frac{L}{\sqrt{\frac{2 \cdot Q \cdot V_{ext}}{m}}} = L \sqrt{\frac{m}{2 \cdot Q \cdot V_{ext}}} \quad (3.2)$$

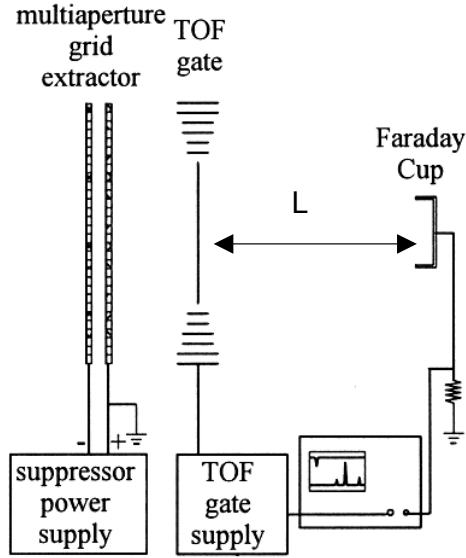


Figure 3.1 Time-of-flight charge-to-mass spectrometer.[1]

From Equation 3.2, it is evident that t is proportional to the inverse square-root of charge-to-mass. If therefore L is large enough as to separate the different species, the result is a current vs time signal where the different ions can be specified as shown in Figure 3.2. To convert the current signal into plasma concentration, the peak intensity of an ion has to be divided by its charge.

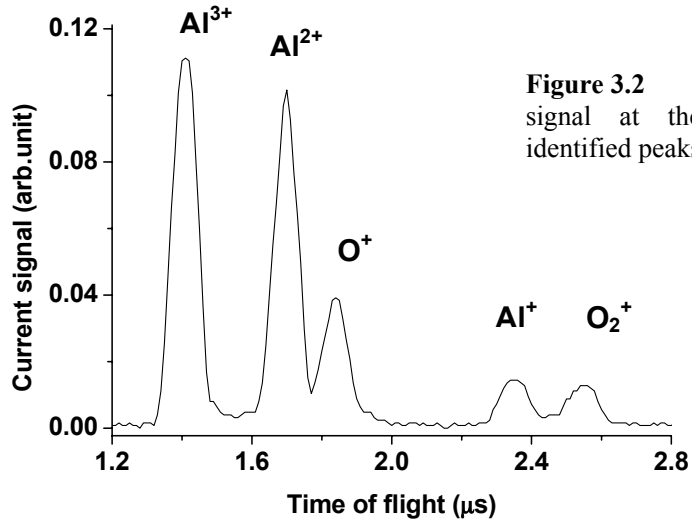


Figure 3.2 Example of current signal at the Faraday cup, with identified peaks.

3.1.2 Mass-energy analyzer

The DC arc plasma was evaluated with a mass-energy analyzer (MEA), which allows investigation of positive and negative ions, neutrals, and their corresponding energies. Basic principles of the analyzer are shown in Figure 3.3.

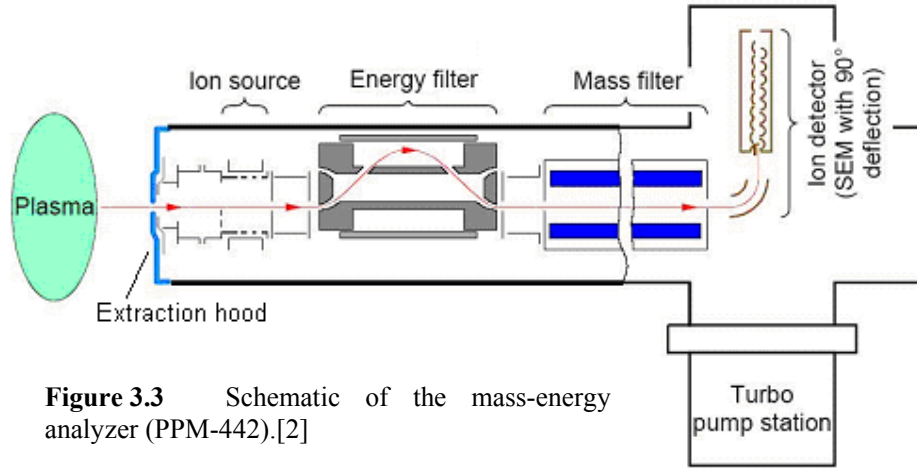


Figure 3.3 Schematic of the mass-energy analyzer (PPM-442).[2]

The particles to be analyzed enter through the entrance orifice (extraction hood). If measuring neutrals, they are first ionized in an ion source zone. The subsequent (electrostatic) energy filter and mass filter (quadrupole field), select ions with a specific energy and ions of a particular mass-to-charge ratio, respectively. The filtered ion current is thereafter deflected 90° and detected after amplification with a secondary electron multiplier. Examples of resulting mass / energy scans are shown in Figure 3.4, where the relative intensities correspond to particle fraction (concentration), assuming identical transport efficiencies for all mass-to-charge ratios.

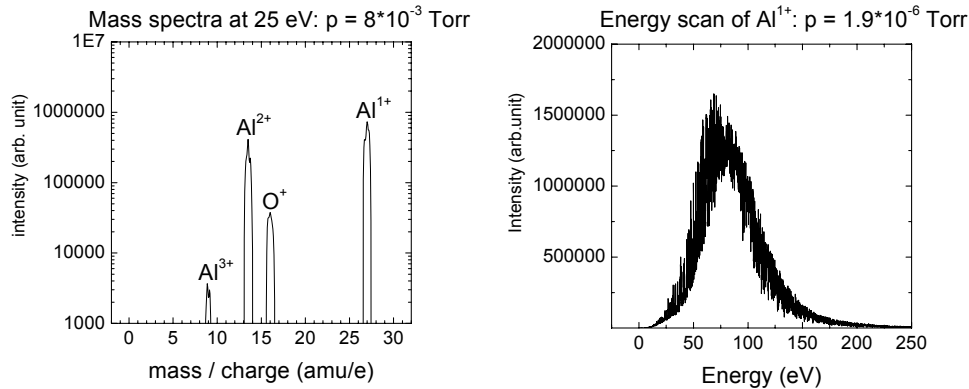


Figure 3.4 a) Example of mass-to-charge signal with identified peaks.
b) Example of measured ion energy distribution.

3.2 Plasma chemistry

Control of the ion energy and its effect on the thin film growth may be achieved through control of the plasma chemistry and charge state distribution, according to the approximate expression in Equation 1.1. The investigations presented below are therefore relevant for both pulsed and continuous cathodic arc plasma sources, in connection to film structure evolution during growth.

3.2.1 Fluctuations

Experimental as well as theoretical data describing the plasma composition and the resulting average ion charge states of vacuum arc plasmas are available for more than 50 cathode materials.[3] Despite the fact that thin film compound synthesis by cathodic arc is usually achieved in the presence of reactive gas as well as magnetic fields, the effect of these process parameters on the fluctuations of the ion species distribution in the plasma have not been investigated so far. Since the film structure and consequently the film properties are determined by these process parameters, one question needs to be answered:

- Is the plasma composition a function of time, in a pulse-to-pulse comparison, as well as within the pulse?

The plasma chemistry - time dependence for a pulsed Al arc in an oxygen environment has here been investigated, where the pulse-to-pulse fluctuation (as shown in Figure 3.5) of the plasma chemistry was quantified at different magnetic field strengths. A schematic of the measurement strategy is shown in Figure 3.5, with analysis of the plasma chemistry using the TOF spectrometer.

For four different magnetic field strengths (between 0 and 0.28 T), a series of 100 TOF spectra was measured, and the concentrations of Al^{1+} , Al^{2+} , and Al^{3+} calculated. From the statistical analysis of these data one can learn about plasma chemistry fluctuations with a resolution of 200 ns. The fluctuation is expressed as relative standard deviation of the averaged 100 individual concentration measurements, S_{rel}

$$S_{rel} = \frac{S}{\bar{x}} = \frac{1}{\bar{x}} \cdot \sqrt{\frac{\left(\sum_{i=1}^n x_i^2\right) - n \cdot \bar{x}^2}{n-1}} \quad (3.3)$$

S is the standard deviation, n is the number of measurements of the concentration x_i , and $\bar{x}$ is the average concentration.

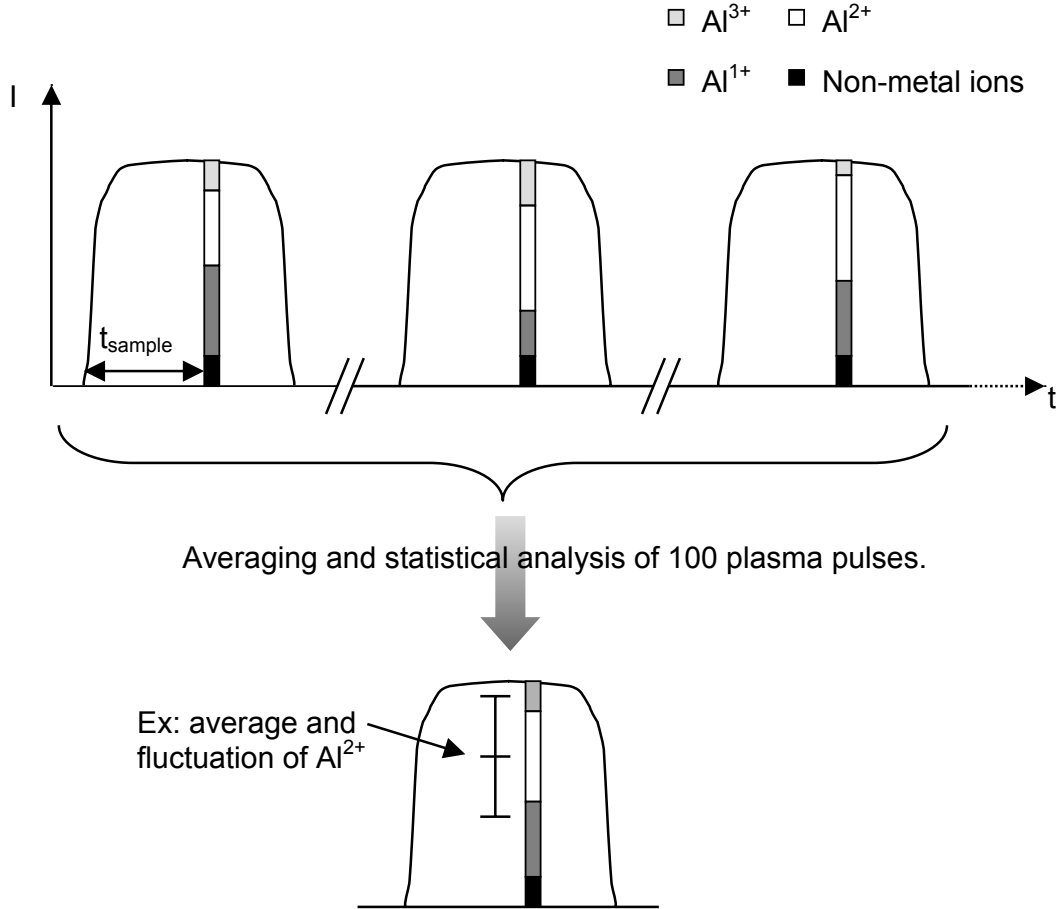


Figure 3.5 Plasma pulses with measured plasma chemistry at t_{sample} into the pulse (top), the results represented by the bars. The pulse-to-pulse fluctuation is evident, also shown in the averaged pulse (bottom).

As can be seen in Figure 3.6, the magnetic field strength strongly affects the pulse-to-pulse fluctuations: Without magnetic field, S_{rel} for Al^+ , Al^{2+} , and Al^{3+} equals 4, 7, and 26 %, respectively. As the magnetic field is increased up to a maximum of $B=0.28$ T, S_{rel} increases drastically to values of up to 46, 66 and 91 %, respectively.

Additionally, the arc burning voltage was measured, i.e. the cathode potential with respect to the grounded anode. Again, a statistical analysis was performed with

100 pulses per parameter set. It was found that an increase in magnetic field strength causes an increase in a) the average burning voltage as well as b) the fluctuations of the burning voltage, which is shown in Figure 3.7. Since the arc current is kept constant this implies that a) the power invested in the cathode surface is increasing with increasing magnetic field strength (B) and b) the fluctuation of the power is also increased with increasing B . These fluctuations are due to the well-known non-stationary character of cathodic arc spots,[4,5] i.e. the rapid formation and extinction of plasma production centers.

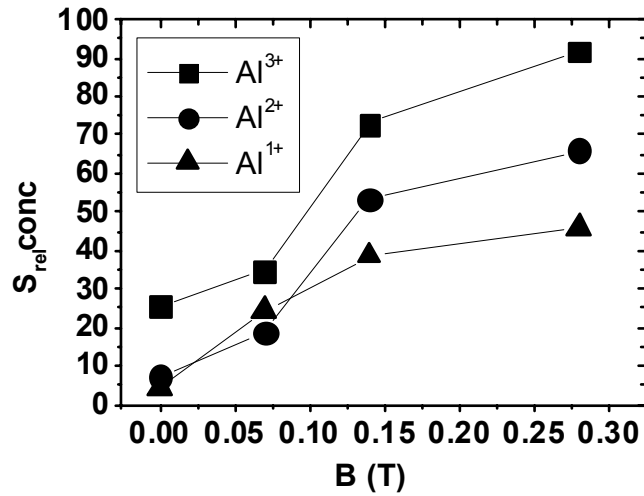


Figure 3.6 Relative standard deviation of aluminum ion concentrations vs magnetic field strength, each data point is based on 100 plasma pulses.

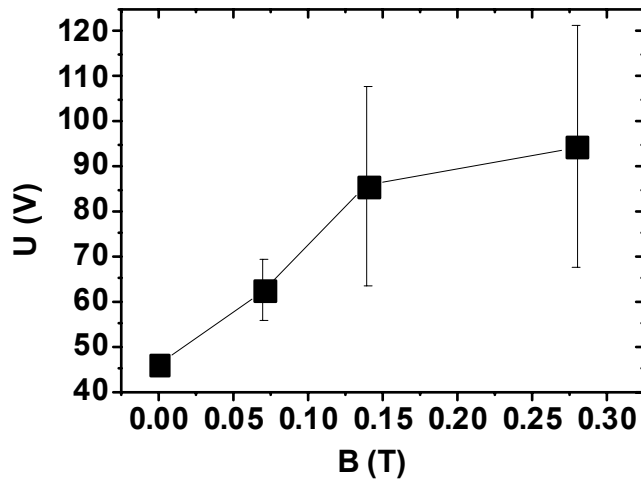


Figure 3.7 Average burning voltage vs magnetic field, the bars represent standard deviation based on 100 plasma pulses per measuring point.

As the power invested in the cathode spot increases, the electron temperature increases,[6] which in turn affects the plasma composition. The correlation of electron temperature and plasma composition for an equilibrium plasma is given by the Saha equations,[7] which used in the model of partial local Saha equilibrium[8] (PLSE) implies division of the plasma in distinct zones (a transition zone) characterized by stepwise “freezing” of the ion charge states (see Chapter 2.3). This model is verified for *vacuum* arc discharges [7,8] but can be used to qualitatively explain findings in reactive gases.

Fluctuations of the burning voltage represent fluctuations of the power invested in the plasma, and therefore the plasma parameters such as the electron temperature exhibit fluctuations as well. Since the ratios of ion concentrations are coupled to plasma density and electron temperature, the *fluctuations* of electron temperature must be associated with *fluctuations* of the freezing conditions in the transition zone and the resulting charge state distribution. A magnetic field increases the range of fluctuations (Figure 3.6). The reason for the increase of fluctuations is not precisely known but it is reasonable to consider that the step distance between explosion centers is increased,[4,5] thereby ion assistance in spot formation is reduced. This would cause the impedance to go through larger amplitude variations. Additionally, impedance fluctuations are more likely to be amplified in magnetized plasmas than in non-magnetized plasmas.[9]

It has been shown here that the reactive plasma cannot be controlled due to the inherent *fluctuations* connected to the process and the physics of cathodic arc spots, but these are also parameter dependent and can therefore possibly be minimized. These findings have implications on the ability to control the ion energy during deposition: The fluctuations of the plasma chemistry will result in a corresponding fluctuation of the ion energy distribution.

3.2.2 Temporal development

In the presence of residual as well as intentionally introduced gas, the plasma chemistry and ion charge states can be affected through changes of the cathode surface chemistry,[10-12] and through interaction between the expanding plasma and the surrounding gas.[13-16] The investigations presented in this section will first deal with effects of a contaminated cathode surface and later focus on effects of plasma-gas interaction.

A: Effects of compound layer formation

In cathodic arc, the plasma originates from cathode spots, which exhibit an unstationary behavior and depend strongly on the surface chemistry. Since the cathode surface is the feedstock material for the plasma, investigation of the latter can give information of the surface composition.

The vacuum arc plasma composition and the average ion charge states of most conductive elements have been measured by Brown and Godechot [17] and theoretically simulated by Anders.[7] Similar experimental investigations have also been performed in the presence of a reactive gas. For example, Oks *et al.* [13] reported reduced ion charge states of Al as the oxygen pressure increased, and Spädtke *et al.* [18] showed the influence of nitrogen pressure on Mo, Fe and Ti ion currents. The investigators have obtained similar results showing that both the concentration as well as the average charge state decreases as the pressure is increased. These data, however, were collected in the steady-state regime of the arc pulse with a delay of $\geq 100 \mu\text{s}$ with respect to arc ignition,[13,17] or correspond to the ion current resulting from integration of the total arc pulse.[18] To see the effect of a compound layer formed in the presence of a reactive gas, a time-resolved analysis is needed.

Very limited data are available describing the temporal development of a cathodic arc. Anders and Jüttner [19] observed a temporal change of the plasma composition in measurements of the ion energy. Schneider *et al.* [12] reported the temporal development of a pulsed aluminum plasma stream at various oxygen pressures. These data suggest that the plasma chemistry and the average Al charge state are strong functions of both oxygen pressure and time into the pulse. The results were explained by the formation and erosion of a compound layer at the cathode surface.

In this study, the temporal evolution of the plasma chemistry in the presence of nitrogen has been analyzed, using cathode materials of Zr and Cr. The analysis of the plasma composition was carried out using time-of-flight charge-to-mass spectrometry, where the plasma composition was calculated from measurements as exemplified in Figure 3.8.

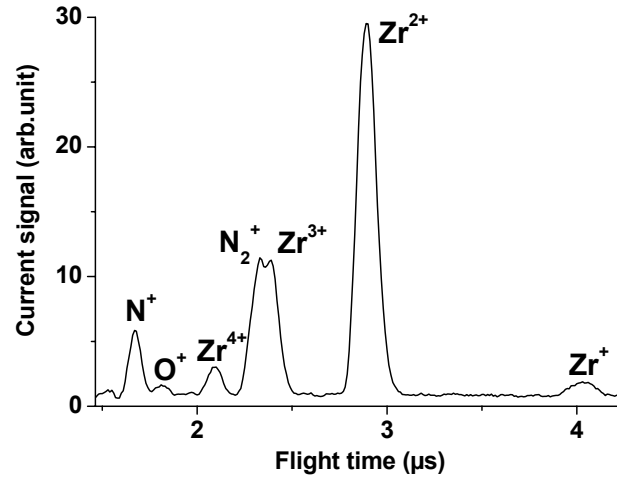


Figure 3.8 Ion current versus TOF, measured at 40 μs into the pulse and at a nitrogen partial pressure of $5 \cdot 10^{-5}$ Torr.

To obtain temporal resolution, the 200 ns sample selected by the TOF gate was scanned through the arc pulse, see Figure 3.9. Time zero was chosen to be the time when the first ions from the arc pulse reached the extraction system, approximately 10 μs after arc ignition, thus corresponding to the beginning of the beam pulse. Using an adjustable delay generator for the TOF, the pulse was scanned in time steps of 5 μs (within the first 30 μs), 10 μs (up to 100 μs) and finally in steps of 25 and 50 μs .

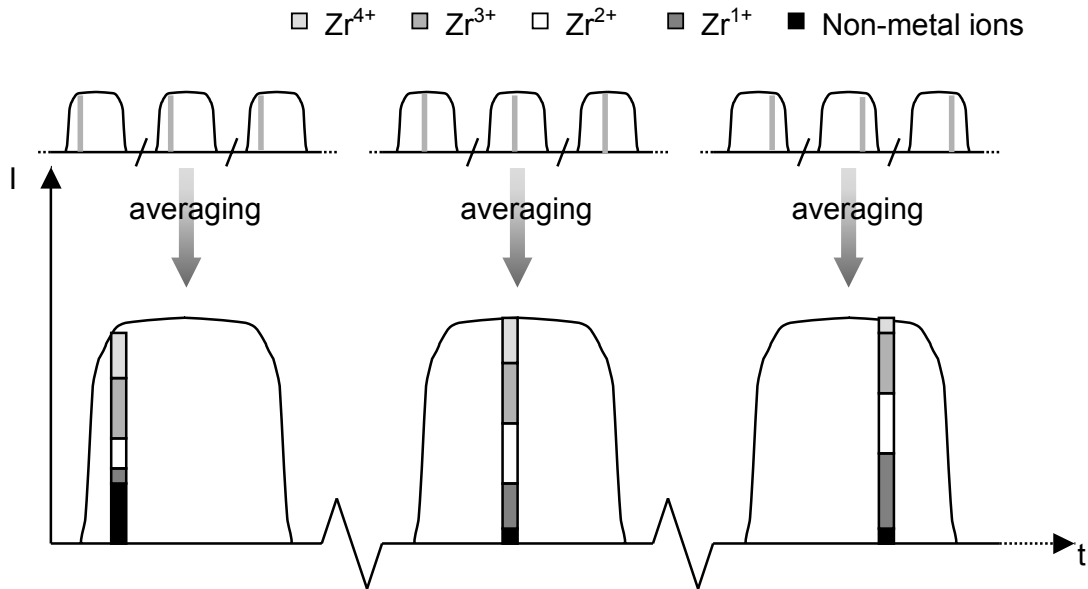


Figure 3.9 Averaged plasma pulses, and in those, measurements of the plasma chemistry *at different times* within the pulse. As in Figure 3.5, the bars represent the plasma chemistry, and show a temporal development of the plasma composition.

The data were collected at a base pressure of $8 \cdot 10^{-7}$ Torr, and after introducing nitrogen up to four different levels, the highest corresponding to a partial pressure of $1 \cdot 10^{-4}$ Torr. For the measurements described, data was collected in the form of averages, where ~ 25 arc pulses resulted in a stabilized average. First, the most relevant results for Zr will be presented in detail, followed by more briefly discussed results of Cr.

In Figure 3.10, the average charge state of Zr is shown as a function of time and nitrogen pressure, calculated from the measured individual Zr ion charge state distributions. At lower pressures the average charge state is strongly dependent on time, the largest changes being within the first 100 μ s. The extreme case is found at a pressure of $5 \cdot 10^{-6}$ Torr, where the average charge state decreases from 3.1 in the beginning of the pulse to 2.4 at the end of the pulse. As the pressure is increased the time dependence becomes less pronounced and the average charge state gradually decreases. At $1 \cdot 10^{-4}$ Torr a steady state is reached at a charge state of 1.9. For a detailed analysis of charge state evolution, i.e. changes in average charge state, see Chapter 3.2.2 B below.

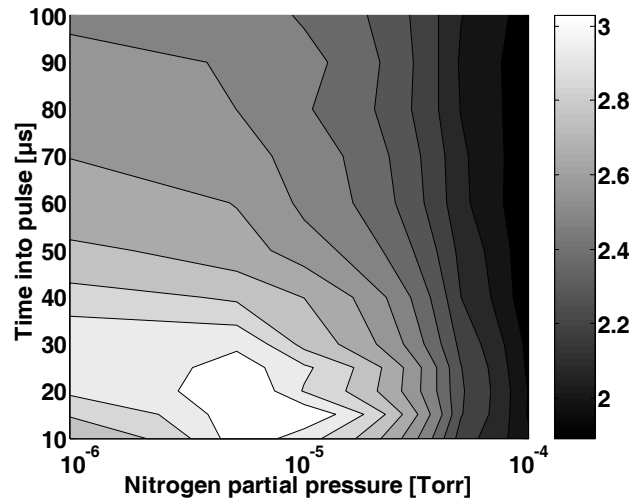


Figure 3.10 Average ion charge state of Zr vs nitrogen pressure (Torr) and time into arc pulse (μ s).

The plasma contained Zr, N and O ions. Small traces of H were also observed, but a meaningful quantification was not possible due to a signal close to noise level. Figure 3.11-3.13 show the Zr, N and O plasma composition, respectively, in at.% of the total plasma composition. All compositions are given versus time into pulse and

nitrogen partial pressure. Only the first 100 μs are shown since the time after that represents the steady-state regime of ion formation where no significant changes are detected (measured up to 250 μs). All three graphs show a strong temporal dependence of the plasma composition, extending over the entire pressure range measured and concentrated within the first 60 μs of the pulse. At low pressures the plasma consisted of Zr, N and O, both N and O most clearly seen within the first 30 μs , with values of up to 30-40 % and 10 % respectively. The relative amount of oxygen never exceeded 10 %, and as the pressure increased, the traces of oxygen decreased in amount as well as in how far into the pulse the traces are seen. This is in contrast to nitrogen, which increased up to 60 % at 25 μs and at a pressure of $5 \cdot 10^{-5}$ Torr. The high nitrogen content also extended further into the pulse; for higher pressures the nitrogen content was 20 % up to 50 μs , before it decreased to approximately 5 %.

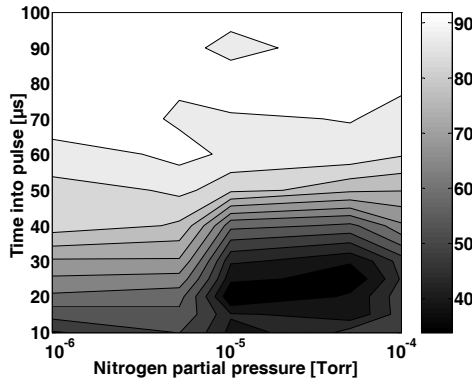


Figure 3.11 Zr ion concentration in the plasma (%) vs nitrogen pressure (Torr) and time into arc pulse (μs).

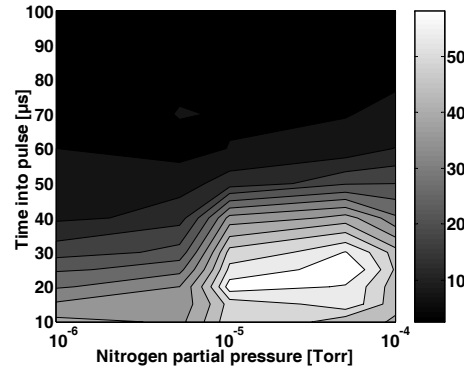


Figure 3.12 N ion concentration in the plasma (%) vs nitrogen pressure (Torr) and time into arc pulse (μs).

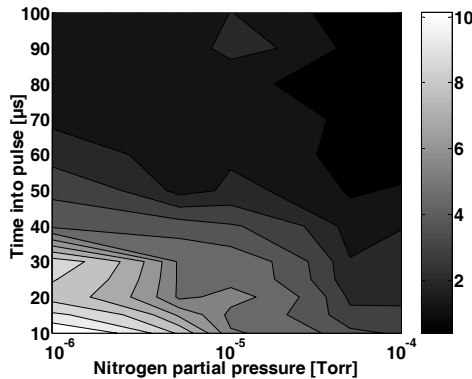


Figure 3.13 O ion concentration in the plasma (%) vs nitrogen pressure (Torr) and time into arc pulse (μs).

The effect of a reactive gas on plasma production in a cathodic arc process can be subdivided into: (a) the interaction at the cathode surface and its immediate vicinity, and (b) the interaction in the plasma expansion volume. In the absence of a magnetic field (a) has been observed to dominate the plasma composition evolution.[20]

Since the pressure in the spot exceeds atmospheric pressure by orders of magnitude, the presence of a gas affects the spot processes indirectly. Depending on gas and cathode material, chemical reactions may occur at the cathode surface, forming a compound surface layer, also referred to as a poisoned layer. The surface temperature associated with plasma production in cathodic arc spots may facilitate chemical diffusion, affecting the thickness of the compound layer.

Kühn *et al.* [11] investigated the surface chemistry of Zr, Cr, and Ti cathodes operated in a nitrogen atmosphere. Using Rutherford Backscattering Spectrometry (RBS) measurements on samples cut from worn cathodes (operated in nitrogen gas), information on average concentration and depth distribution of nitrogen was obtained, as listed in Table 3.1. For Zr, the results were 16 at.% in a nitride layer of average thickness $\leq 0.1 \mu\text{m}$. Ref. 11 therefore indicates that a nitrided layer is formed.

Metal	T_{melt} (K) [21]	T_{plasma} at cathode spot (eV) [7]	RBS-measurement of cathode (at.% N) [11]
Zr	2128	3.7 (~43000 K)	16 in depth $\leq 0.1 \mu\text{m}$
Cr	2180	3.4 (~39000 K)	Under detect. limit

Table 3.1 Cathode materials and selected properties.

A compound surface layer affects both the spot ignition mechanism and the plasma production process, as compared to a clean surface. One distinguishes between spots of type 1 (occurring on contaminated surfaces) and of type 2 (on clean surfaces), see Chapter 2.2. On a contaminated surface the dielectric layers favor the formation of new spots. As a result, an increasing number of type 1 spots tend to show random movement over larger distances as compared to type 2 spots on clean surfaces.[4,9,22-23]

The temporal development of the plasma composition versus nitrogen partial pressure reported here for Zr can be explained in terms of the cathode surface

chemistry and associated implications for the cathode spot motion: At base pressure, the cathode surface reacts chemically with both nitrogen and oxygen, stemming from residual gas.[12,20] As the arc is ignited, the cathode spot runs over the surface and erodes this layer, resulting in a time dependent plasma chemistry evolution in the beginning of the pulse. The existence of type 1 spots depends on surface state and volume of nitrided / oxidized material. After approximately 60 μ s, the arc burns on bulk material and a steady state regime is reached. As the nitrogen pressure increases, the oxygen concentration gradually decreases while the nitrogen concentration increases. According to Ref. 11 a nitrided layer is formed at the Zr cathode surface. Therefore, spots of type 1 will prevail in the beginning of the arc pulse. Since these spots run preferentially over the nitrided area, the compound layer will be eroded first, followed by a transition to type 2 spots, which erode the clean Zr surface.

As the nitrogen partial pressure is increased, the nitrogen concentration-time distribution increases both in amplitude and width, as shown in Figure 3.12. This can be understood in terms of diffusion occurring at the cathode surface, which may result in the formation of a thicker nitrided layer and / or a layer changing in composition towards higher nitrogen content as the pressure increases. One crucial parameter affecting the formation of this compound layer is the pulse repetition rate,[24] the time available between the pulses for the cleaned surface to regain its previous nitrided state. Another parameter of great importance is the size of the cathode surface, since it affects the ability to form a new nitrided layer *during* the pulse, in areas already cleaned by the cathode spots.

For discussing the evolution of the compound layer chemistry and hence the plasma composition, we need to consider both energetics and kinetics. Gibb's free energy of formation ΔG , the enthalpy of formation ΔH , and possible phase changes for the nitrides taken from literature, are given in Table 3.2.

Nitride	ΔG (kJ/mol) [25]	ΔH (kJ/mol) [26]	Phase changes
ZrN	-377	-365	M: 3250 K [27]
Cr₂N	-150	-128	D: ~1900-2000 K [28]
CrN	-133	-125	D: ~1970 K [26]

Table 3.2 Stable nitrides formed from the cathode materials investigated. M=melting, D=decomposition.

ΔG and ΔH are temperature dependent (in Table 3.2 given at room temperature), and so is the diffusion constant D_N of nitrogen in the cathode material. The temperature distribution of the cathode surface is not well defined. The temperature field extends from the temperature of the cooling water in the bulk of the cathode, to $\sim 43\,000\text{ K}$ at the Zr cathode spot (the plasma temperature), as seen in Table 3.1. Very steep temperature gradients into the cathode both with respect to geometry and time can be expected. The magnitude of the temperatures involved suggests that the activation energies for the diffusion processes can be overcome. The nitrogen diffusion constant measurements reported in the literature are characterized by large scattering, and for Zr (in the solid state) D_N is limited to $1\cdot 10^{-9}\text{ mm}^2/\text{s}$ (extrapolated data).[29] Generally, as the temperature approaches the melting temperature of the material, the curve of D_N might exhibit a small upward curvature, as compared to the extrapolated line, followed by an increase in the diffusion constant of several orders of magnitude in the liquid at the melting temperature.[30,31]

Based on the above considerations with respect to energetics and kinetics we suggest that the cathode surface chemistry is affected by diffusion processes. This is consistent with the strong temporal development of the concentration gradients observed in Figure 3.11-3.13.

A pressure and temporal dependence of both the plasma chemistry and the average charge state were found also for Cr, though not as pronounced. Cr plasma showed a maximum concentration of nitrogen ions of $\sim 20\%$ measured at $1\cdot 10^{-4}\text{ Torr}$ nitrogen gas pressure, which decreased gradually during the first 30-40 μs down to a nitrogen ion fraction of $\sim 5\%$, which was the steady state value. When the pressure was decreased, the time dependence was less pronounced, and below $1\cdot 10^{-5}\text{ Torr}$ steady state was reached. The average ion charge state of Cr showed qualitatively the same development as for Zr, with a maximum of 2.6 in the beginning of the pulse at lower pressure and a minimum of 1.6 in the steady state regime at the highest pressure, as seen in Figure 3.14.

The discussion above explaining the time- and pressure dependence of the plasma originating from a Zr cathode is qualitatively consistent with the data measured for Cr plasma streams. The investigation in Ref. 11 included also Cr as a cathode material, where the nitrogen concentration was found to be under the detection limit. Our investigation suggests the existence of a compound layer on Cr,

but only at higher nitrogen pressures. Both metals show a similar pressure dependent effect; erosion of a nitrided layer at the cathode surface causing a temporal dependence of the plasma chemistry. A Zr cathode results in the highest nitrogen content in the plasma, while Cr has not as high levels.

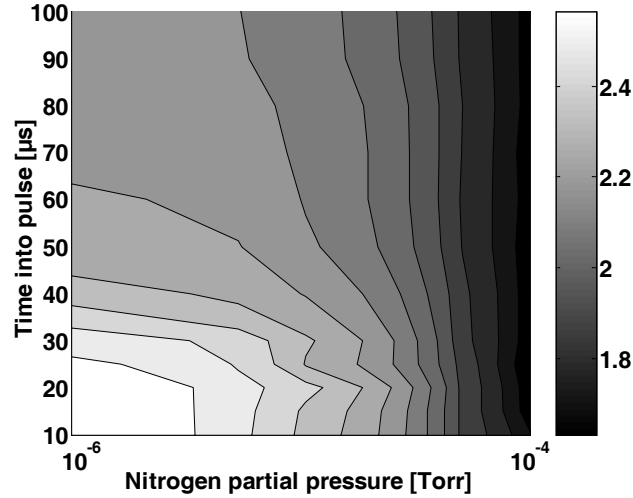


Figure 3.14 Average ion charge state of Cr vs nitrogen pressure (Torr) and time into arc pulse (μs).

For pressures below $1 \cdot 10^{-5}$ Torr, Zr shows a strong temporal dependence with up to 40 % of nitrogen in the beginning of the pulse. In the same pressure range Cr shows hardly any temporal dependence at all with the steady state value of 5 %. If the cathode surface chemistry could be based on energetics, Zr would be the most nitrided material, but the result of Cr would be more pronounced, see Gibb's free energy of formation in Table 3.2. A measurable effect of nitridation for Cr would then be expected. As the pressure increases, nitrogen concentration gradients are found also for Cr, though the detected levels for Zr are 2-3 times higher. Our measurements together with the RBS-measurements in Ref. 11 therefore suggest that the nitridation of the surface is based on *both* energetics and kinetics.

A direct comparison of the diffusion constants of the materials is not straight forward, due to insufficient experimental data (though the extrapolated limitation for D_N in Zr and Cr is approximately the same) as well as the unknown temperature distribution of the cathode surfaces. The calculations of the plasma temperature in the cathode spot (Table 3.1) may indicate that the surface temperature peak of the Zr cathode is somewhat higher, probably resulting in higher diffusion of nitrogen in Zr as

compared to Cr. What should also be considered is the difference in how sensitive the materials are to temperature changes and nitride formation. Zr and Cr have approximately the same melting temperature, but behave differently when forming nitrides. The nitrides of Cr are more sensitive to temperature as compared to Zr, since they decompose at temperatures lower than the melting point of the pure metal. Zr on the other hand forms a nitride that melts more than 1000 K above the melting temperature of pure Zr. Therefore, in order to discuss the chemical diffusion more thoroughly, one needs to know both the temperature distribution and the diffusion mechanisms present, both in the pure cathode materials and the nitrides formed.

These results for Zr and Cr in nitrogen are qualitatively consistent with the explanation given in Ref. 12 for Al in oxygen. Therefore, a temporal development of the plasma composition, caused by the formation and erosion of a compound layer, seems to be a general effect of a reactive gas in a pulsed cathodic arc process. To what extent it can be expected depends on the material and its reactivity, and also on parameters like arc current, pressure, geometry of the cathode and pulse repetition rate, as mentioned above. A similar temporal dependence may also be expected in plasma processes other than cathodic arc, especially other pulsed processes.

B: Effects of plasma-gas interaction

In the presence of a gas, the plasma composition and average charge state is affected by various collision phenomena, like charge transfer, ionization and recombination. The influence of a reactive gas has been investigated; for example Martin *et al.* [32] investigated the photon and ion emission from a titanium cathodic arc plasma at varying nitrogen pressure, and Demidenko *et al.* [33] and Sakaki *et al.* [34] analyzed the influence of pressure on the ionization and excitation mechanism of Ti and Mo, and Ti arc plasma, respectively. Ionization phenomena and ion current signal were also investigated by Kimblin [35] for varying cathode materials and different gases. The results of these investigators show a decrease of higher charge states and ion current signal with increasing pressure, and an increase in gas ion fraction. This was explained primarily by charge exchange reactions between metal plasma ions and surrounding gas atoms or molecules, but also by electron impact ionization of gas.

No *charge-state-resolved* data on the *temporal dependence* of the plasma chemistry can be found in literature. However, such data is required since the energy

gain in the sheath in front of the substrate is proportional to the individual ion charge state. Therefore, the previous investigation has been extended to include a study of the charge-state-resolved plasma composition, both with respect to its temporal development as well as the influence of surrounding pressure. These results are of importance to reactive plasma processing, especially to pulsed processes utilizing substrate bias, since varying plasma chemistry translates to difficulties of controlling the compositional as well as the microstructural evolution of the film.

The experimental details correspond to those described in Chapter 3.2.2 A. The time-of-flight system was differentially pumped, with the pressure in the cathodic arc zone about a factor 35 higher than in the TOF zone. It should be noted that with differential pumping and an extraction voltage of 30 kV, the probability for changes in the beam composition is very limited due to the very short beam transport times after extraction.

The 250 μs plasma pulse can be divided into two phases, namely before and after about 150 μs into the pulse, where the latter represents approximately a steady state in the plasma chemistry evolution. The former will hereafter be referred to as the transient phase, characterized by extensive changes in the plasma chemistry, both in time and with pressure. Most of the discussion will therefore deal with the transient phase.

Transient phase; low pressure, $p < \sim 10^{-5}$ Torr

For the present investigation, the average charge state in Figure 3.10 is resolved into its individual charge states, which gives more detailed information of plasma evolution. At low pressure, $p < 10^{-5}$ Torr, the beginning of the pulse is dominated by Zr^{4+} ions (up to $\sim 20\%$ within the first 50 μs) and Zr^{3+} (up to $\sim 45\%$, highest level is in the time period $\sim 50\text{-}100\ \mu\text{s}$), see Figure 3.15-3.16. The balance is given by Zr^{2+} , Zr^{1+} , N_2^+ , and N^+ , see Figure 3.17-3.20. Small traces of oxygen ions were also detected (see Figure 3.13) but are not further discussed here.

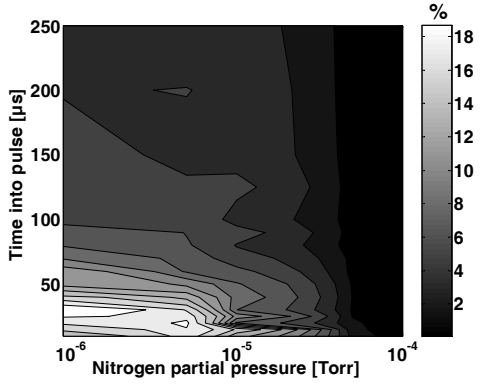


Figure 3.15 Concentration (particle%) of Zr^{4+} ions vs nitrogen pressure (Torr) and time into arc pulse (μs).

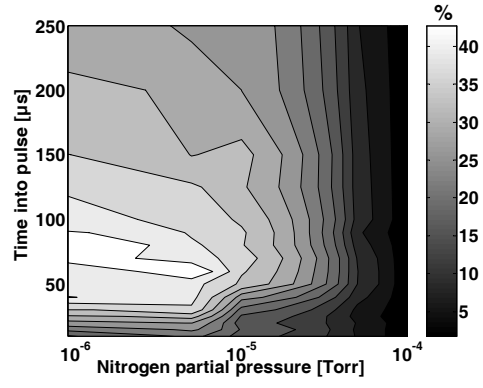


Figure 3.16 Concentration (particle%) of Zr^{3+} ions vs nitrogen pressure (Torr) and time into arc pulse (μs).

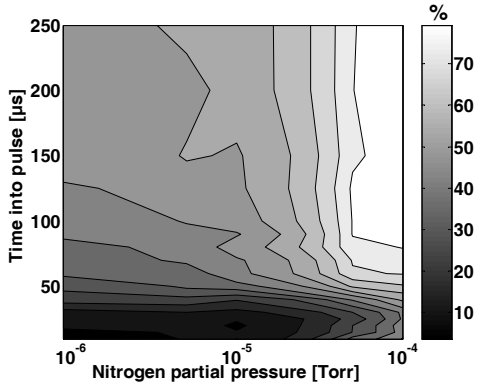


Figure 3.17 Concentration (particle%) of Zr^{2+} ions vs nitrogen pressure (Torr) and time into arc pulse (μs).

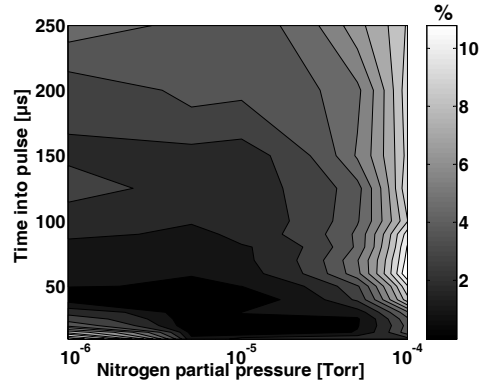


Figure 3.18 Concentration (particle%) of Zr^{1+} ions vs nitrogen pressure (Torr) and time into arc pulse (μs).

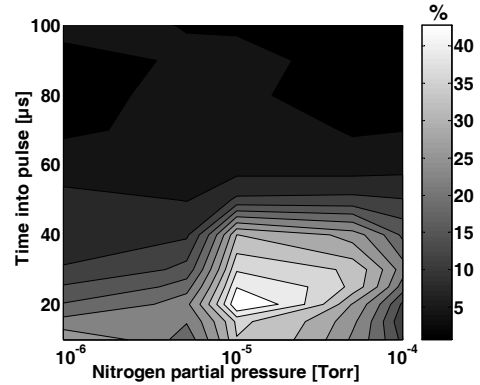


Figure 3.19 Concentration (particle%) of N_2^+ ions vs nitrogen pressure (Torr) and time into arc pulse (μs).

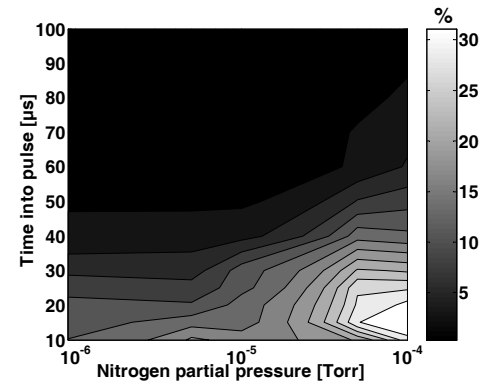


Figure 3.20 Concentration (particle%) of N^+ ions vs nitrogen pressure (Torr) and time into arc pulse (μs).

Anders and Yushkov [36] reported higher ion charge states and higher ion velocities at the beginning of each arc pulse. The higher ion velocities corresponded to more than twice the steady-state average ion kinetic energy. As long as the arc current was rising, the arc burning voltage was higher than in steady-state. These observations indicate that more energy is invested per plasma particle in the beginning of the arc pulse, and therefore available also for ionization. As the plasma expands into the chamber, it can do so without suffering from many collisions with gas molecules at this low pressure.

Transient phase; elevated pressure, $p > \sim 10^{-5}$ Torr

As the pressure increases to 10^{-5} Torr and higher, large changes in plasma composition were measured within the first ~ 50 μ s of the pulse: An abrupt decrease in the fraction of Zr^{4+} and a more gradual decrease of Zr^{3+} , combined with an increase in N_2^+ , as seen in Figure 3.19. This behavior is consistent with an increased interaction between the expanding metal plasma and the surrounding gas through asymmetric charge transfer (reactions between unlike systems)



where Me^{x+} stands for the x-fold charged metal ion. The nitrogen molecule may dissociate in these processes. Written as individual reactions, one should consider



The cross sections for reactions of this type are vastly different because of the internal energy defect, ΔE , which is the difference in potential energies (ionization, excitation) between pre-collision and after-collision particles. If the energy defect is negative, $\Delta E < 0$, the cross section is negligibly small. Reactions (3.5) – (3.8) and (3.10) have $\Delta E < 0$. The remaining reactions are much more likely to occur, leading to a sharp

reduction of Zr^{4+} and Zr^{3+} while increasing the fraction of lower zirconium charge states and forming nitrogen ions, in particular N_2^+ .

The theory of charge exchange involves a transient stage, as does three-body-recombination. When a multiply charged ion approaches an atom in a ‘slow’ collision, as is the case in our plasma, a transient, excited “molecule” is formed. An electron from the neutral target is state-selectively captured by the multiply charged ion in a certain distance from the neutral target atom, typically 0.3-0.6 nm. State selection is determined by a matching condition of the potential energy of the initial and final channel in a reaction window. While classical trajectory Monte Carlo (CTMC) method [37,38] was found to be adequate in many instances, little is known about the specifics on zirconium charge exchange with nitrogen.

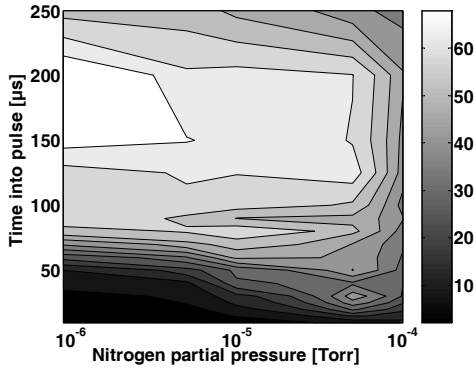


Figure 3.21 Signal proportional to number of ions (all species) detected vs nitrogen pressure (Torr) and time into arc pulse (μs).

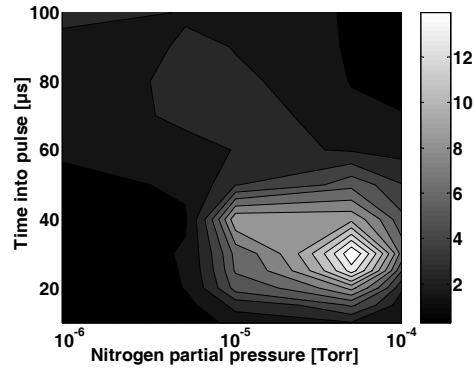


Figure 3.22 Signal proportional to number of N_2^+ ions detected vs nitrogen pressure (Torr) and time into arc pulse (μs).

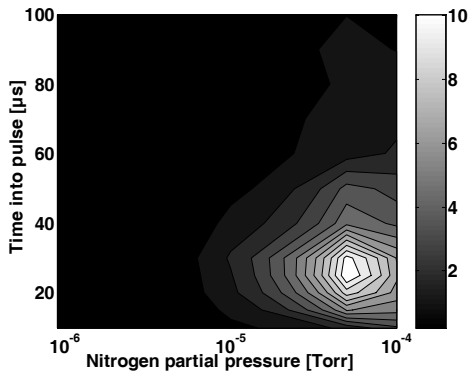


Figure 3.23 Signal proportional to number of N^+ ions detected vs nitrogen pressure (Torr) and time into arc pulse (μs).

With an increase in pressure above $\sim 3 \cdot 10^{-5}$ Torr, the fraction of N_2^+ slowly decreases (Figure 3.19). Since the *total* number of ions detected in the same region

(Figure 3.21) is increased, the decrease is not in contradiction to a measured increase in the number of N_2^+ ions (Figure 3.22). An increase in the number of ions at about 30 μs and $6 \cdot 10^{-5}$ Torr is detected with constant measured ion current. This is consistent with the proposed charge exchange mechanism, resulting in ion charge being distributed over more particles.

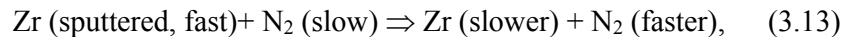
The presented variations in Zr ion and N_2^+ ion fraction are accompanied by an increase in N^+ ion fraction, see Figure 3.20, and increase in N^+ ion signal, see Figure 3.23. The onset of the increase in ion current occurs at higher pressure for N^+ as compared to N_2^+ . (Figure 3.19-3.20 and 3.22-3.23 only show the first 100 μs in the pulse, since no changes after this time were detected.) The N^+ ions are here suggested to originate from a compound layer formed at the cathode surface. This argument is based on considering the cross-sections for the production of N^+ ions. The cross section of dissociative ionization and charge transfer in collisions between metal ions and N_2 is smaller than the cross section for production of N_2^+ . [39] Collisions involving N_2^+ ions are another possible source for N^+ , though the cross sections for the different reactions indicate a low probability for dissociation and formation of N^+ , as compared to collisional reactions that deplete the N^+ population. [40,41]

More support for these suggestions for the origin of the nitrogen ions is found by comparing the measured N_2^+ and N^+ ion signals and calculated ion fractions. Starting with the fractions (Figure 3.19-3.20), the peak of N^+ is found closer to the beginning of the pulse than the peak of N_2^+ . The N^+ fraction extends further into the pulse with increasing pressure, which indicates a thicker nitrided surface layer, or cathode compound layer shifting in composition towards higher nitrogen content. The extension of the N_2^+ fraction into the pulse does not change up to the highest pressure range investigated. Turning to the measured signals of the two gas ion species (Figure 3.22-3.23), a comparison shows smoother gradients for the N^+ signal, which is more focused towards the beginning of the pulse and higher pressures. Previously published results [12] and discussed data (Chapter 3.2.2 A) suggested a compound layer on the cathode due to the presence of reactive gas ions. The results should be considered in light of these charge-state-resolved measurements. It is appreciated that the gas ion signal can be composed of both a molecular part and an atomic part, of which only the latter indicates the presence of a compound layer at the cathode surface. The increment of ion current towards the beginning of the pulse with increasing pressure is also indicative for the formation and erosion of a compound layer. The reason is a

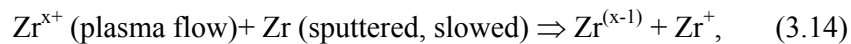
faster and more stable (less fluctuating) arc ignition / plasma formation process that reaches steady-state faster as the surface is increasingly nitrided.[19]

Charge exchange collisions with neutral metal atoms are usually neglected with the argument that the plasma is fully ionized, with the fraction of neutrals being very small. This is consistent with the finding [7] that ion charge state distributions usually peak at charge state 2+ or 3+. However, recent research on a cathodic arc system similar to the present system identified an additional source of neutral metal atoms in the vacuum arc case, namely self-sputtering of metal in the energetic condensation process on walls and substrate.[42] In essence, the very energetic ions produced in a cathodic arc discharge show a likelihood to sputter an atom from the surface they are condensing onto. Both kinetic and potential energy of ions contribute to a total energy supply per incident ion that significantly exceeds the typical surface binding energy.[43] The sputtered atom is most likely a metal atom of the same kind, originating from previously condensed material. As with most sputtered atoms, a self-sputtered atom has a kinetic energy of typically a few eV, which translates in a characteristic time of 100 μ s for crossing the pre-surface volume of ~ 0.1 m dimension. In light of these recent results, the increase of metal neutrals and their interaction with the fully ionized plasma flow from the cathodic arc source appears to contribute to the transitional phase ($t < 150 \mu$ s) and the establishment of the quasi-continuous steady state phase ($t > 150 \mu$ s).

While self-sputtered metal was identified to also be responsible (at least in part) for the temporal development of charge state distributions in the vacuum case,[42] the effect is even more pronounced in the presence of gas. In the vacuum case, the density of sputtered metal atoms remained low in the pre-surface volume due to the relatively high energy (eV). With increasing gas pressure, sputtered Zr atoms suffer collisions with gas atoms,



which reduces their average velocity and enhances their density. This, in turn, increases the probability that metal ions from the cathode will make a charge exchange collision,



which successively reduces the concentration of higher charged Zr ions while increasing concentrations of doubly and singly charged Zr ions (Figure 3.15-3.18).

Steady state phase

The steady state phase ($t > 150 \mu\text{s}$) is characterized by an almost constant total ion current signal, which is only slightly decreasing as the pressure increases (though, one should always keep in mind that *averaged* values are measured and discussed, while instantaneous values show rapid fluctuations due to the explosive nature of plasma production). At low pressures, $p < \sim 10^{-5}$ Torr, more than 40 % of the plasma ions are Zr^{4+} and Zr^{3+} . As the pressure is increased to $p > \sim 10^{-5}$ Torr, the particle concentrations of Zr^{4+} and Zr^{3+} gradually decrease and the populations of Zr^{2+} and Zr^{1+} increase, as shown in Figure 3.15-3.18. In the steady state phase, the total fraction of nitrogen ions was less than 2 % over the entire pressure range investigated.

The observed combination of 1) a strong pressure dependence of the metal charge states and 2) a comparatively low fraction of gas ions throughout the gas pressure range, is most likely due to the interaction of self-sputtered material with the background gas, followed by metal ion – atom charge exchange, as already explained for the transitional phase.

In addition, three-body-collisions, where electrons (e^-) recombine with metal ions (Me^{x+}) according to



may also contribute, however, the probability for the two-body collisions exceeds the probability of three-body reactions. The recombination reaction (3.15) is most efficient with electrons as the third body.[34] The corresponding three-body recombination rates are known to sensitively depend on the electron temperature, namely approximately as $T^{-9/2}$ for electrons of a few eV.[44,45] No quantitative information is available at this time on reduction of electron temperature due to interaction with background gas and ions. While the gas temperature is close to room temperature, ions cannot not be simply described by a temperature due to the high directed velocity of metal ions coming from cathode spots.[46] The coupling of electrons with heavy particles via elastic collisions must therefore be considered as dependent on the species. The transfer of kinetic energy in a collision between an energetic electron (few eV) and a “cold” molecule is inefficient because its scales with the small factor $2m_e/M$, Ref. 47. The cross section for elastic collisions between electrons of a few eV energy and nitrogen molecules is about $1.5 \cdot 10^{-19} \text{ m}^2$, Ref. 48, exceeding inelastic cross sections by a large factor. Using the cross section, density estimates, and energy transfer factor, one can quickly see that electron cooling by

elastic collisions with heavy particles is only effective at high pressure (0.1 Torr and higher), which is higher than the pressure estimated in our source region. These estimates indicate the limited effectiveness of electron cooling and three-body-recombination, and therefore the interaction of self-sputtered material with the gas molecules appears as the most important factor explaining the pressure dependence of the plasma composition for the steady state phase.

The charge state resolved measurements discussed here show both a strong time *and* pressure dependence of the plasma chemistry and ion charge states, indicating large variations in ion energy distribution during film deposition. Comparing pulsed and DC plasma production systems, the latter can be considered as operating continuously in the steady state phase, therefore showing less variation over time. Pulsed systems, going through the transient phase with every pulse, have broader variation of plasma composition and ion energy distributions, which may be acceptable or even advantageous but implies less ability to control film composition and structure.

3.2.3 Residual gas

Vacuum based techniques for film growth are characterized by the presence of residual gas. In high vacuum the residual gas contains mainly water, but for example nitrogen, oxygen and carbohydrates may also be present.[49] These impurities can have a profound influence on the composition and the structure of the films.[50,51] Hence, quantification of the residual gas present here was evaluated with both TOF and MEA techniques.

The presence of residual gas is evident from Figure 3.13, where traces of oxygen are identified for a pulsed Zr arc in a nitrogen environment.

A more detailed analysis has been made for the DC arc, with the MEA in the neutral mode. Neutrals in the chamber are then measured when there is no plasma production, i.e. the results are relevant for both the straight and the curved filter used in the experimental setup. The latter example is shown in Figure 3.24.

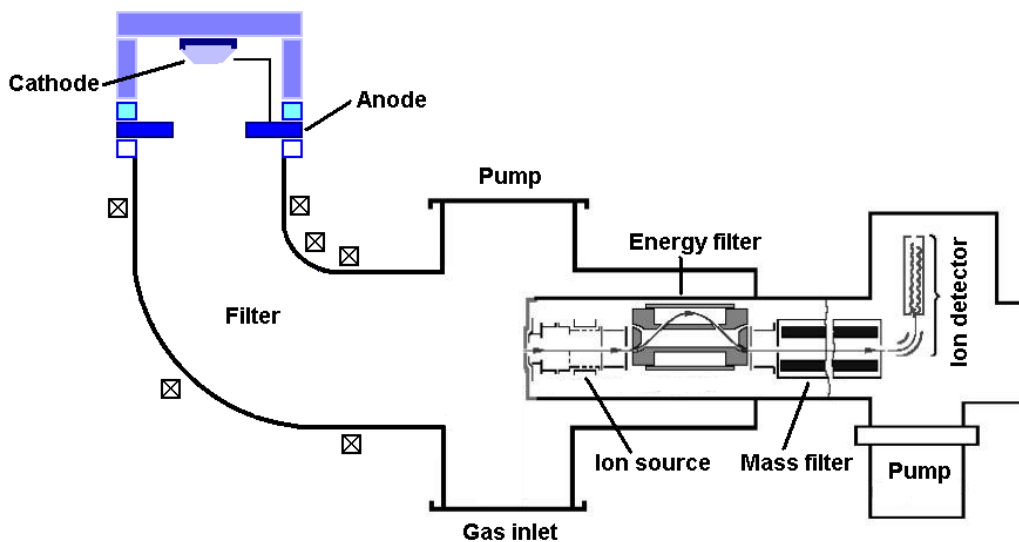


Figure 3.24 Experimental setup with curved plasma filter and the MEA.

When measuring neutrals, electric fields in the MEA are used in order to repel possible positive ions and only include neutrals in the signal (the neutrals are ionized before detection). A resulting mass scan is shown in Figure 3.25, measured at $1.5 \cdot 10^{-6}$ Torr. The identified main peaks show the most abundant ions originating from the residual gas.

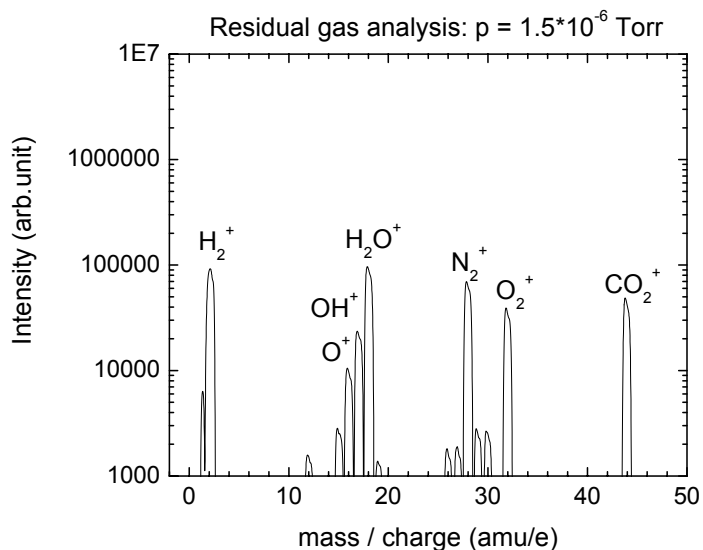


Figure 3.25 Intensity vs mass-to-charge ratio, measured at $1.5 \cdot 10^{-6}$ Torr.

As expected, H_2O together with H_2 , N_2 , CO_2 and O_2 are the most abundant residual gases in the high vacuum ambient. The water generally originates from the ambient water, and the water induced by plasma stimulated desorption from the chamber walls.

A previously reported TOF spectrometry investigation has shown an increasing hydrogen content in the plasma with increasing oxygen partial pressure.[50] Therefore, a residual gas analysis was performed also at the pressure chosen for the film depositions (see Chapter 4 and Chapter 5), $\sim 4 \cdot 10^{-3}$ Torr. The result can be seen in Figure 3.26, where the intentionally introduced O_2 shows the largest intensity. Most abundant residual gases are H_2O , N_2 and H_2 , with the intensity of the H_2O peak being 1 % of the one for O_2 . Consequently, incorporation of impurities during thin film synthesis may be expected, and the above gained information is useful when correlating film formation with synthesis conditions.

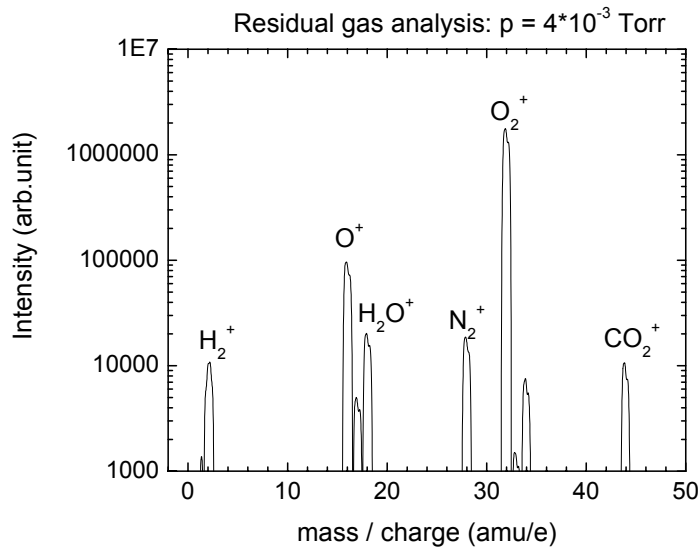


Figure 3.26 Intensity vs mass-to-charge ratio, measured at $4 \cdot 10^{-3}$ Torr (oxygen environment).

3.3 Ion energy distributions

3.3.1 High vacuum

Vacuum arc plasma is well known to be highly ionized with high directed ion energies (averages for most materials are between 20 and 150 eV).[36] These properties have importance for synthesis of dense coatings with the possibility to control their structure evolution. Most energy studies deal with the average or the most likely ion energy in the plasma, or they describe ion energy *distributions* (IEDs) averaged over all ion species present.[46,52-55] The experimental data available on the dependence of the IED on ion charge state is rather limited.[56-63] Davis *et al.*[57] and Miller [58] showed an increasing ion energy with increasing charge, while Bugaev *et al.*,[59,60] Yushkov *et al.*,[61] Galonska *et al.*,[62] and Chhowalla [63] reported that energy distributions are approximately independent of ion charge state.

Several theories have been suggested to account for ion acceleration mechanisms leading to the energies observed. The two most referred to are the potential hump theory [52] and the gasdynamic model.[64] The former predict ion formation near a peak of the discharge voltage profile (see Figure 2.8) and acceleration due to the electric field, and the latter states that electron-ion friction and expansion cooling (pressure gradient) are the main mechanisms responsible. Adjustments to these models [65,66] and further investigations [61,67] have been made but there is still a lack of reliable, charge-state-resolved IEDs data.

The production of so-called macroparticles is an inherent drawback of utilizing cathodic arc sources for thin film growth. To strongly reduce the amount of these particles, various filtering methods are used.[68] The most frequently applied approach is to utilize curved magnetic fields,[69] see Chapter 2.3.2. It has been shown that an external magnetic field influences the discharge and plasma properties such as fluctuations (see Chapter 3.2.1),[70] plasma chemistry [20] and ion charge state distributions.[71] There are also published data available describing the effect of magnetic field strength for a straight magnetic field configuration on the ion kinetic energy.[36] However, the data are not charge-state-resolved, and they give no information about the *distribution* of ion energies.

Here, detailed measurements and analysis of charge-state-resolved IEDs of metal ions present in aluminum vacuum arc plasma are presented. The experimental

distributions are fitted with shifted Maxwellian distributions, where the fitting parameters may provide information on the plasma properties. Three different configurations are studied; free plasma expansion in the absence of a magnetic field, plasma expansion in the presence of a straight solenoid magnetic field, and plasma expansion in a curved field.

Vacuum arc plasma was generated from a conical aluminum cathode (base and top diameters 51 and 12 mm, respectively, and height 38 mm), powered by a direct current (DC) arc supply, with resulting arc current of 35 A. The arc was triggered by a voltage flashover across a ceramic tube between a trigger electrode and the cathode. The cathode spots were confined to the cathode surface by a permanent ring magnet located behind the cathode. All measurements were performed in oil-free vacuum at a base pressure of about $3 \cdot 10^{-6}$ Torr, with three different magnetic field configurations: Plasma expansion in a straight duct was studied in the absence and presence of a magnetic field, see schematic of the experimental setup in Figure 3.27. The magnetic field was generated with a coil of 400 turns and a current of 15 A, which served as the plasma filter. The estimated magnetic field strength in the filter was 40 mT, which is in the range generally used for plasma filtering. Plasma expansion in a curved duct (90°) was also studied, using the similar but curved coil setup.

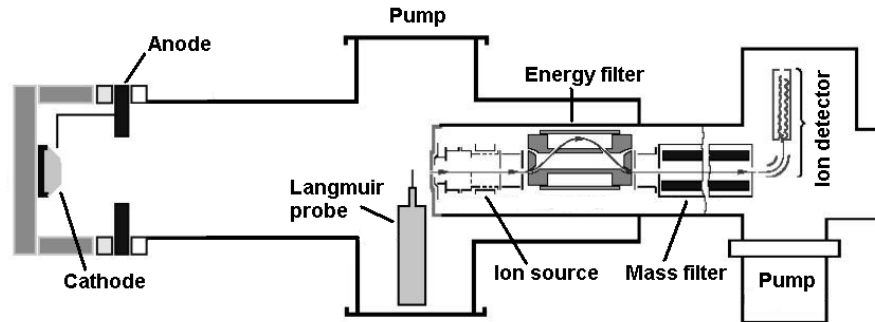


Figure 3.27 Schematic of the experimental setup.

For the straight filter with no field applied, initial plasma characterization was carried out using a Langmuir probe in the form of a 10.25 mm long Pt wire exposed to the plasma. The plasma potential was found to be positive, approximately 3 V with respect to the anode (ground). The Langmuir probe was retracted for IED measurements, where a mass-energy analyzer (PPM-422, Pfeiffer Vacuum) was used

to determine plasma chemistry through a mass-to-charge measurement at fixed energy, and IEDs through energy measurements at fixed mass-to-charge ratio. The entrance orifice of the mass-energy-analyzer was grounded.

The raw data from measurements using a straight duct with no magnetic field applied is shown in Figure 3.28. In order to represent a smoothened IED with no high frequency fluctuations in the distribution, Fourier components with frequencies higher than $\Delta t/n$ were removed, where n is the number of data points considered at a time, and Δt is the spacing between two adjacent data points. In the IED, every 1-eV step is divided in 16 data points, and smoothening was done over a range of 5 eV.

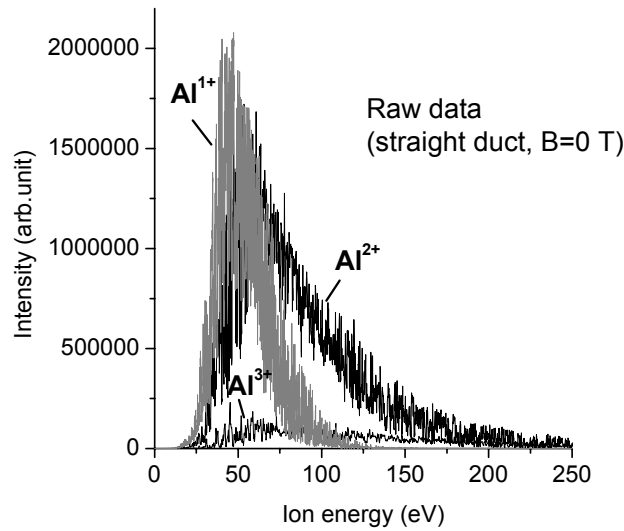


Figure 3.28 Measured ion energy distributions for a straight duct with no magnetic field applied (raw data).

A: Straight duct, no magnetic field

A mass-to-charge measurement at 50 eV, showed Al^{1+} , Al^{2+} , and Al^{3+} as the most abundant ions, as well as small traces (intensity less than 1% of the metal ion signal) of hydrogen, oxygen and nitrogen ions. Consequently, measurements of IEDs were limited to the three metal ions. The smoothened IEDs are shown in Figure 3.29, where one can see slight differences between the different ions. In accordance with some previous reports in literature,[57,58,72] higher charged ions show higher energies; the measured (uncorrected) averages correspond to 54, 88 and 120 eV for Al^{1+} , Al^{2+} and Al^{3+} respectively. If one includes a charge-dependent correction due to ion acceleration over the orifice sheath potential difference, the resulting average

energies change to 51, 82, and 111 eV. The reproducibility of this fundamental result was shown in four repeated series of measurements. Each time the same trend was observed: The difference in average energy between Al^{1+} and Al^{2+} was in the range 27 ± 4 eV, and the corresponding difference between Al^{2+} and Al^{3+} was 28 ± 2 eV. The previously reported total velocity distribution function for Al extends up to a velocity corresponding to approximately 225 eV,[46] which is consistent with the here measured distributions, see Figure 3.29. Furthermore, the calculated average charge state is 1.7, also consistent with literature.[36]

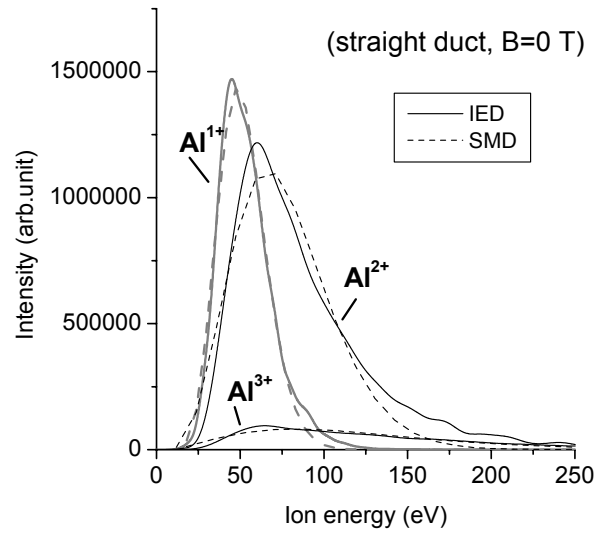


Figure 3.29 Smoothened IEDs (of raw data in Figure 3.28) with fitted shifted Maxwellian distributions (SMD). Measured using a straight duct with no magnetic field applied.

Neither the potential hump theory nor the gasdynamic theory can by itself explain the here-observed charge-dependent differences of the IEDs, namely that *higher* average energies exist for *higher* charged ions: The average energies are neither proportional to the charge state (potential hump) nor approximately equal (gasdynamic model neglecting electron-ion coupling). Furthermore, higher charged ions are more accelerated if also electron-ion coupling (Q^2 dependence) contributes to ion expansion and acceleration.[65] The accelerating potential predicted by the potential hump theory is on the order of a few volts, and hence the greatest contribution to ion acceleration seems to be the pressure gradient in conjunction with electron-ion coupling, as previously suggested in theoretical models.[65,66]

To gain additional information on the plasma parameters, the distributions were fitted by shifted Maxwellian distributions (SMD), as done by Kutzner *et al.*[56] Bilek *et al.*[15] also adopted this approach to describe IEDs of Ti^+ ions in a nitrogen environment. The forward ion flux distribution of a SMD can be written as

$$f(E) = C_s [E - QV_p] \cdot \exp\left[-\left(\sqrt{E - QV_p} - \sqrt{E_{dir}}\right)^2 / T\right] \quad (3.16)$$

where C_s is a scaling constant, V_p is the plasma potential with respect to the reference voltage of the analyzer (0 V = ground), E_{dir} is the directed energy (center-of-mass energy) of the ions, Q the charge state, and T is the temperature (or random energy). The terms containing Q are introduced to correct for the increase in ion energy due to the difference between plasma potential and analyzer entrance (ground). C_s , E_{dir} , and T were varied as to obtain the best fits (minimized error function) to the measured IEDs.

Figure 3.29 shows that the IEDs can be well described by shifted Maxwellian distributions, with fitting parameters as presented in Table 3.3. Since only the forward flux of the ions is measured, the fitting parameters indicate the contribution of directed energy (E_{dir}) and width of the distribution (temperature T) to the average energy. For approximately the same temperature (width of the distribution), a higher average energy corresponds to a higher directed energy. Comparing the parameters of Al^{1+} and Al^{2+} , one can see that the higher average energy of Al^{2+} is due to both a higher directed energy and a broader distribution. The even higher average energy of Al^{3+} is primarily due to a high temperature (broad distribution).

	Al^{1+}	Al^{2+}	Al^{3+}
E_{ave} (eV)	51	82	111
QV_p (eV)	3.0	6.0	9.0
E_{dir} (eV)	40.9	46.2	26.8
T (eV)	2.3	7.4	28.9
C_s	33329	20885	1660

Table 3.3 Average energy (E_{ave}), ion charge (Q) times sheath potential difference (V_p) and fitting parameters (directed energy E_{dir} , temperature T , scaling constant C_s) used in Eq. (1) to fit the measured IEDs for a straight duct with no magnetic field.

The difference in directed energy as well as temperature between Al^{3+} on one hand and Al^{1+} and Al^{2+} on the other hand, may be explained by charge exchange collisions. Recent findings [42] have shown that neutrals are present in cathodic arc plasmas; the sources are not only evaporating macroparticles and hot craters but self-sputtering that occurs when energetic ions condense on substrates and walls. Collisions with these neutrals will cause some of the highly charged ions to cascade down to lower charge states. Since the plasma is dominated by Al^{1+} and Al^{2+} , the charge exchange collisions will be most observable from a change in the IED of Al^{3+} . It has previously been reported [15] that interaction (including charge transfer) between expanding plasma and gas molecules resulted in decreasing peak energies of the IEDs with increasing pressure, but with accompanying difficulties to eliminate energetic ions in the high energy tail. Correspondingly, charge transfer reactions between neutrals and Al^{3+} will mainly result in a decreased maximum intensity of the Al^{3+} IED, while the high energy tail is maintained. The shifted Maxwellian distribution will become broader, which is equivalent to a higher temperature. It should be stressed that the ion temperature is a formal assignment of a parameter to the *time-averaged* IED, and that the temperature of a momentary distribution is much smaller. In a previous study, the broadening of averaged distributions due to the fluctuating character of momentary distributions was presented.[8]

B: Straight duct, with magnetic field

To investigate the effect of a magnetic field on the charge-state-resolved IEDs, the same setup as described in the previous section was used, the only difference being an applied magnetic field ($B = 40$ mT) in the duct. The resulting smoothened IEDs together with fitted shifted Maxwellian distributions are shown in Figure 3.30, with corresponding fitting parameters in Table 3.4. One should note the difference in energy scale from Figure 3.29. An increase in concentration of higher charged ions as the magnetic field is applied is evident. An increase in average kinetic energy is also observed, corresponding to 30, 75 and 122 eV for Al^{1+} , Al^{2+} and Al^{3+} , respectively, which is approximately proportional to the charge state. The starting points of the IEDs measured with and without a magnetic field do not show any significant difference, and hence the assumption is made that the plasma potential is approximately equal for all measurements. Otherwise there would be a charge-dependent shift of the IED starting point due to ion acceleration over the potential

difference between plasma potential and grounded entrance orifice of the analyzer. Consequently, the measured increase in average ion energy cannot be explained by acceleration in the orifice sheath.

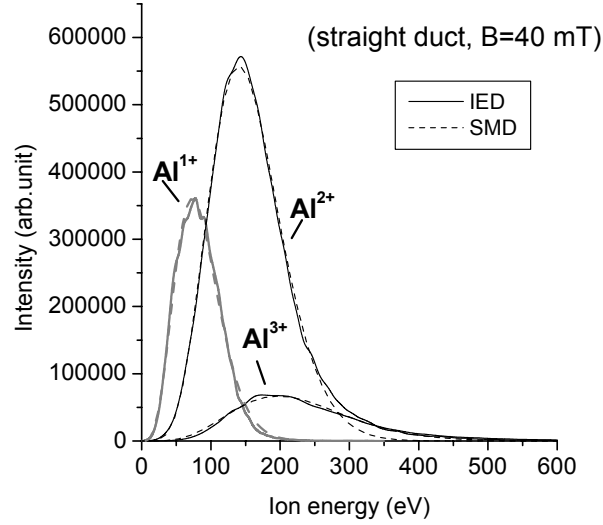


Figure 3.30 Smoothened IEDs with fitted shifted Maxwellian distributions (SMD). Measured using a straight duct with magnetic field applied.

	Al^{1+}	Al^{2+}	Al^{3+}
E_{ave} (eV)	81	157	233
QV_p (eV)	3.0	6.0	9.0
E_{dir} (eV)	55.3	114.0	152.3
T (eV)	8.0	10.6	19.1
C_s	5741	4498	391

Table 3.4 Average energy (E_{ave}), ion charge (Q) times approximated sheath potential difference (V_p) and fitting parameters (directed energy E_{dir} , temperature T , scaling constant C_s) used in Eq. (1) to fit the measured IEDs for a straight duct with magnetic field.

Measurements of the potential difference between anode and cathode (the burning voltage V_{arc}) showed an increase from 26 to 42 V as the field was applied. This is explained by an enhanced impedance of the discharge when the electrons emitted from the cathode travel across magnetic field lines. It is well known that a

higher input power (see Equation 2.3) increases the electron temperature and the ion charge states,[71] and as shown here, also the charge-state-resolved ion energy. This result is consistent with Ref. 36, reporting an increase in arc burning voltage and total average kinetic energy with increasing magnetic field strength.

The fitting parameters in Table 3.4 indicate that the kinetic energy is increased as the magnetic field is applied. This is due to a combination of a higher directed energy and broader distribution (higher T) for Al^{1+} , and mainly due to a higher directed energy for Al^{2+} and Al^{3+} . The observed charge state dependence of the acceleration motivates a more detailed analysis of possible specific acceleration mechanisms, which will be discussed below.

C: Curved duct, with magnetic field

The effect of the discharge configuration was investigated using a similar but 90°-curved coil. The field strength was again $B = 40$ mT. In Figure 3.31, the smoothened and fitted IEDs are shown, with fitting parameters as presented in Table 3.5. The plasma potential was assumed to be approximately unchanged from the previous setup, motivated by the starting points of the IEDs, see section B. There is a slight increase in average and directed energy from the previous case, but apart from that no significant effect of filter on the IEDs was observed. Consequently, also here ion acceleration seems to be charge-state dependent.

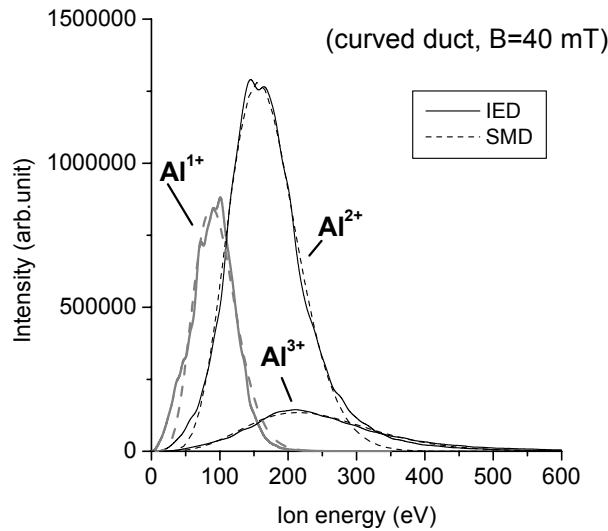


Figure 3.31 Smoothened IEDs with fitted shifted Maxwellian distributions (SMD). Measured using a curved duct with magnetic field applied.

	Al^{1+}	Al^{2+}	Al^{3+}
E_{ave} (eV)	89	168	250
QV_p (eV)	3.0	6.0	9.0
E_{dir} (eV)	73.3	133.1	164.9
T (eV)	5.9	8.6	21.3
C_s	10740	9058	729

Table 3.5 Average energy (E_{ave}), ion charge (Q) times approximated sheath potential difference (V_p) and fitting parameters (directed energy E_{dir} , temperature T , scaling constant C_s) used in Eq. (1) to fit the measured IEDs for a curved duct with magnetic field.

Several investigations of ion transport in straight [73] and curved [74-78] filters have been reported, including both experimental results [73-75] and theoretical models.[76-78] However, most studies concern efficiency of plasma transport, and plasma flow directions. No studies of the effect of magnetic field or field curvature on the charge state resolved energies are available. Still, observations from the above mentioned studies can be used to interpret our results: The magnetic field strengths generally employed in arc plasma filters is not high enough to magnetize the ions, i.e. to make the ion cyclotron radius smaller than the duct radius.[73] However, the electrons are strongly magnetized, and thus effectively confined by the magnetic field. Due to the requirement of a quasi-neutral plasma, the ions are guided by the self-consistent electric field that arises.[76] Additionally, there may be electric fields relative to the plasma at the exit and entrance of the duct.[77] Hence, charge-state-dependent ion acceleration may occur due to electric fields far from the spot in a magnetized plasma. In regions of strong electron pressure gradient, acceleration may also occur due to electron-ion coupling.

The effect of magnetic field configuration on the charge-state-resolved IEDs has not been reported before. These results have large implications for all plasma-based deposition techniques in the presence of magnetic fields, since it is well known that the kinetic energy affects the thin film microstructure evolution, and hence the film properties.[79] Furthermore, it can be concluded that the charge states as well as the ion energies can be manipulated by suitable magnetic field configuration.

3.3.2 Oxygen environment

When a gas is introduced in the chamber, the resulting plasma-gas interactions affect the IEDs. The influence of nitrogen partial pressure on the IED of Ti^+ was studied by Bilek *et al.* [15], and Tarrant *et al.* [80] investigated the charge state resolved average ion energy for a Ti arc in a nitrogen environment. General conclusions were a decrease in energy with increasing pressure.

A series of measurements (experimental setup shown in Figure 3.24) has been performed for an Al arc plasma at different oxygen partial pressures, starting with a mass scan to identify the constituents in the plasma, then followed by energy scans for the most abundant ions. Figure 3.32 shows the calculated average energies for the different ion species, at a pressure between $1.9 \cdot 10^{-6}$ and $8 \cdot 10^{-3}$ Torr.

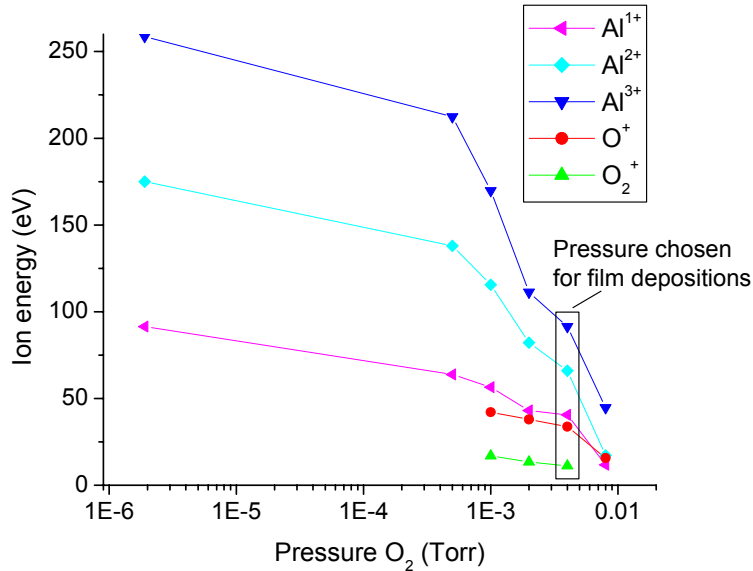


Figure 3.32 Average energy vs pressure (O_2) for the most abundant ions in the Al arc plasma.

As can be seen, the result is consistent with previous findings, and can be understood based on plasma-gas interaction including scattering as well as charge exchange and ionizing collisions (see Chapter 3.2.2).

In order to correlate phase formation with synthesis conditions, the plasma chemistry and ion energy distribution was measured at conditions later employed for thin film growth. A mass scan at 35 eV showed Al^{1+} , Al^{2+} , Al^{3+} and O^+ as the most

abundant ions, as well as traces of molecular oxygen, hydrogen and nitrogen ions (in total less than 1 %), see Figure 3.33.

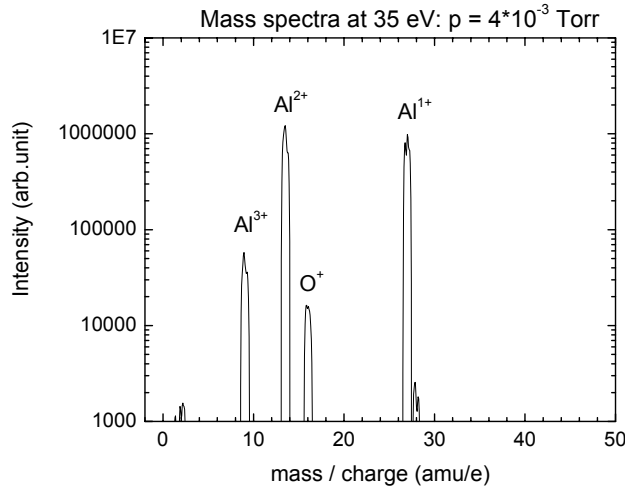


Figure 3.33 Mass scan at 35 eV, measured at $4 \cdot 10^{-3}$ Torr.

Consequently, the here presented IEDs are limited to the metal and atomic oxygen ions, see Figure 3.34. The distribution for Al^{1+} , Al^{2+} and Al^{3+} can be described by an average energy of 41, 66 and 90 eV, and a high energy tail extending above 100, 200 and 250 eV, respectively. Additionally, there is a small but clearly distinguishable distribution of O^{+} , with an average energy of 11 eV.

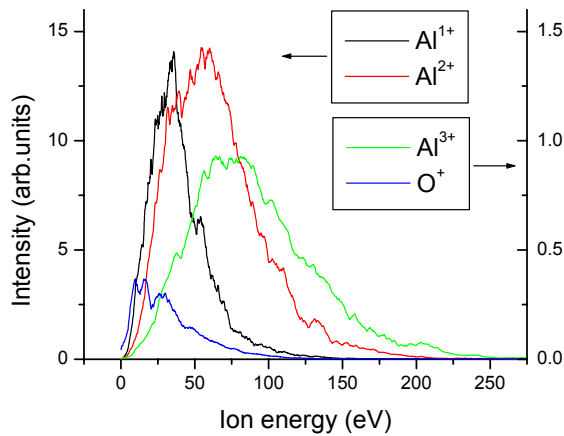


Figure 3.34 Ion energy distributions of Al^{1+} , Al^{2+} , Al^{3+} and O^{+} measured at $4 \cdot 10^{-3}$ Torr (thin film growth condition).

These results indicate that for a substrate bias potential of -50 V, ion energies in excess of 400 eV are attained, both from the high energy tail and the accelerated ions

with $Q > 1$ (see Equation 1.1). In Figure 3.35, the charge dependent ion energy distributions resulting from a substrate bias potential of -100 V is exemplified.

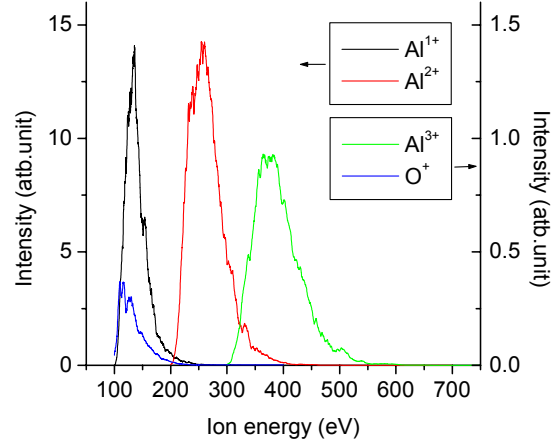


Figure 3.35 The charge dependent ion energy distributions resulting from a substrate bias potential of -100 V.

Correspondingly, under the assumption that the acceleration for the individual charge states are independent, ion energies above 1000 eV are obtained at a substrate bias potential of -300 V.

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4. Thin film growth

This chapter gives a brief description of deposition setup and procedures.

4.1 Experimental setup

The deposition system included a stainless steel vacuum chamber in the form of a cross, length 27 cm and inner arm diameter of 10 cm. The chamber was connected to a fore-vacuum pump (EcoDry M15) and a torbomolecular pump.

The thin film growth was performed using a filtered cathodic arc source, see schematic of the setup connected to the chamber in Figure 4.1. The arc plasma was generated from a conical aluminum cathode (base and top diameters 51 and 12 mm, respectively, and height 38 mm), powered by a direct current (DC) arc supply, with resulting arc current of 35 A. To avoid the incorporation of macro-particles and neutrals in the growing film, the plasma was filtered with a magnetic field, through a coil with 400 turns and a coil current of 15 A, using the same principle as depicted in Figure 4.2.

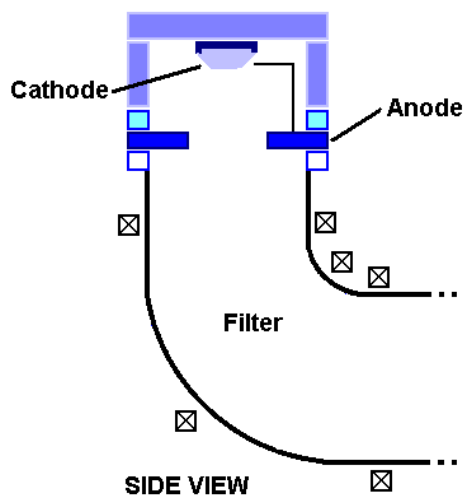
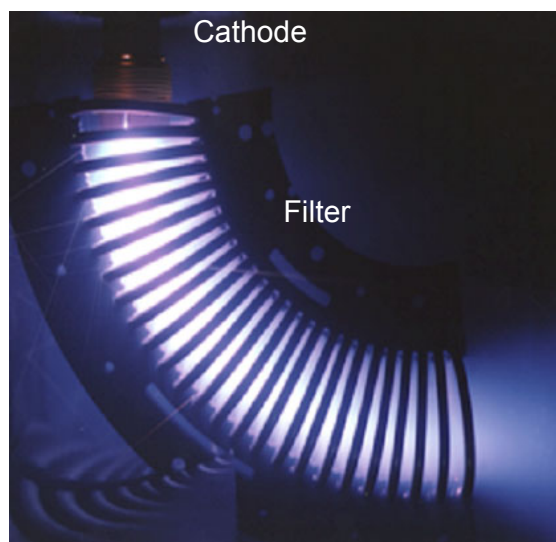


Figure 4.1 Setup of cathodic arc source.

Figure 4.2 Photo of macroparticle filtering.



The films were deposited on V2A stainless steel substrates, located at 14 cm from the exit of the duct, and hence at the previous position of the energy analyzer orifice, see Figure 4.3. The substrate was mounted on a holder which could be heated and electronically biased. Substrate temperature was monitored by means of a K-type (NiCr/NiAl) thermocouple.

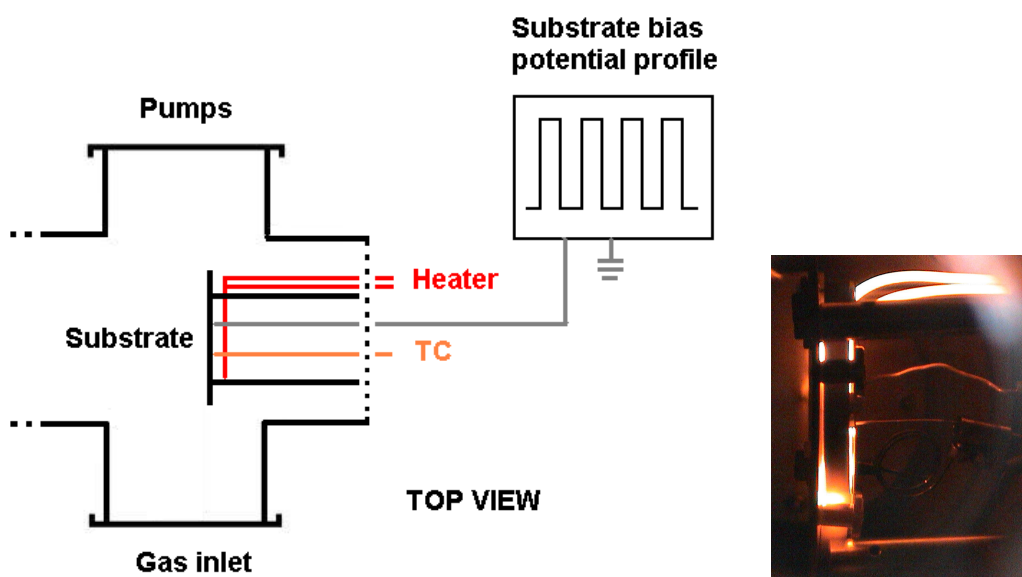


Figure 4.3 Top view (schematic) of the deposition chamber, with corresponding photo of the heated substrate.

4.2 Film deposition

All substrates were ultrasonically cleaned, washed in acetone and dried in a flow of nitrogen. Prior to deposition, the substrate was heated up to the deposition temperature in an oxygen environment. In order to grow stoichiometric thin Al_2O_3 films, the oxygen partial pressure was increased until the formation of Al was suppressed as identified by X-ray diffraction. That pressure, $\sim 3.5 \cdot 10^{-3}$ Torr, was then used for the depositions presented in Chapter 5, at a base pressure of approximately $3 \cdot 10^{-6}$ Torr.

Film growth was made at the substrate temperature and the substrate bias potential varied from 200 to 800 °C and from -50 to -300 V, respectively. The pulse frequency was set to 9.4 kHz, where the substrate bias potential, U_{bias} , was applied for half the cycle, see Figure 4.4. During a deposition the substrate potential U alternated between U_{bias} and the floating potential U_{float} (~ -45 V). The substrate current density J changed correspondingly between 0.02-0.032 (depending on U_{bias}) and ~ 0.01 A/cm², respectively. Depositions at lower substrate bias potentials were not carried out, since a further reduction results in arcing at the substrate. It should be stressed that *average* values of potentials and current densities are discussed, while instantaneous values show large fluctuations due to the non stationary nature of the plasma production.

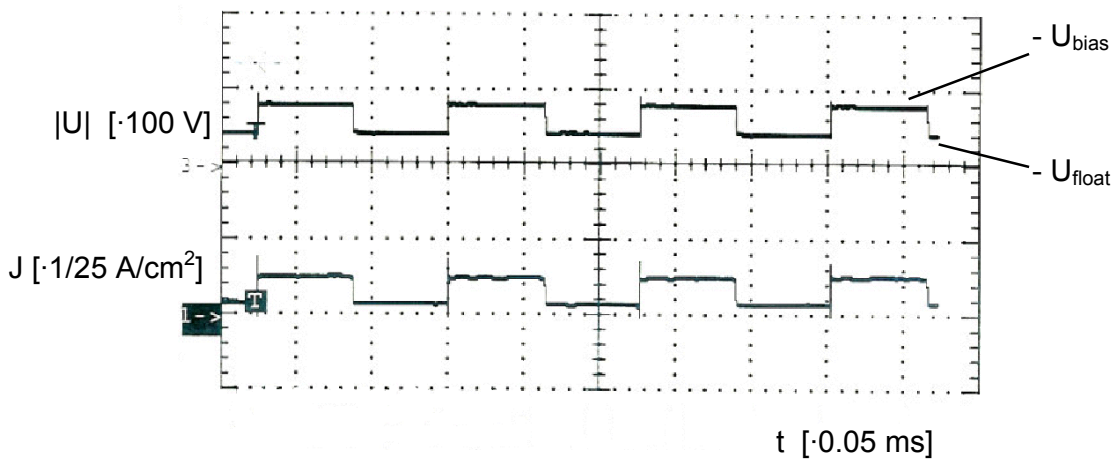


Figure 4.4 Substrate current density (J) and substrate bias potential (U) during deposition.

A pulsed substrate bias potential has previously been shown to be efficient in discharging insulating surfaces and controlling the ion energy.[1] However, varying the substrate bias potential also affects the magnitude of the current to the substrate, and hence the power density. As an example, the power density increased by a factor of approximately 6.7 as the substrate bias potential was changed from -50 to -250 V. It has previously been proposed that both ion flux and ion energy play an important role in the formation of crystalline alumina.[2]

To maintain stable deposition conditions, a new cathode was inserted prior to every second deposition. Therefore, only the topmost layer of the cathode was eroded and changes in the cathode – anode distance were less than 3 mm throughout the study. Different extent of cathode erosion is shown in Figure 4.5, where a new cathode, a cathode after ~ 15 min plasma generation, and a cathode after > 90 min plasma generation is depicted.



Figure 4.5 Cathodes showing different extent of erosion due to plasma generation.

The deposition time was 6 minutes, which resulted in a film thickness of ~ 350 nm (i.e. a deposition rate of ~ 1 nm/s).

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5. Thin film characterization

This chapter contains a brief description of the film characterization techniques used here. Results of the analysis are presented in addition to a discussion concerning the correlation between the previously investigated plasma properties (Chapter 3) and the here presented film properties.

5.1 Techniques

5.1.1 Elastic Recoil Detection Analysis

Composition analysis of a film including light elements (such as hydrogen) can be made with high energy ion beam scattering spectrometry, of which one technique is elastic recoil detection analysis (ERDA).[1] The film is exposed to an ion beam under grazing incidence. The incident ions collide with the atoms in the film, the collisions being considered as purely elastic. By using ions that are heavier than the film atoms, the lighter atoms are knocked forward in the collision and recoil out of the film, see Figure 5.1. Detection of these atoms, after subtraction of possibly scattered ions, provides a method for the depth resolved analysis of the film composition. The mass and energy of the recoiled/scattered particles, are commonly analyzed in a Bragg ionization chamber (which is a gas filled enclosure measuring the

gas ionization current caused by the recoiled species), a time-of-flight detector, and / or a semiconductor detector.

Here, the chemical composition was measured with Cl^{7+} ions incident on the film, at an angle of 15° , and with an energy of 35 eV. Two detectors were applied: a Bragg ionization chamber (BIC) and a Si detector so as to determine the type and the energy of recoils. The BIC acquired all elemental information except for H, which was analyzed by the Si detector. Further details considering the ERDA setup can be found elsewhere.[2]

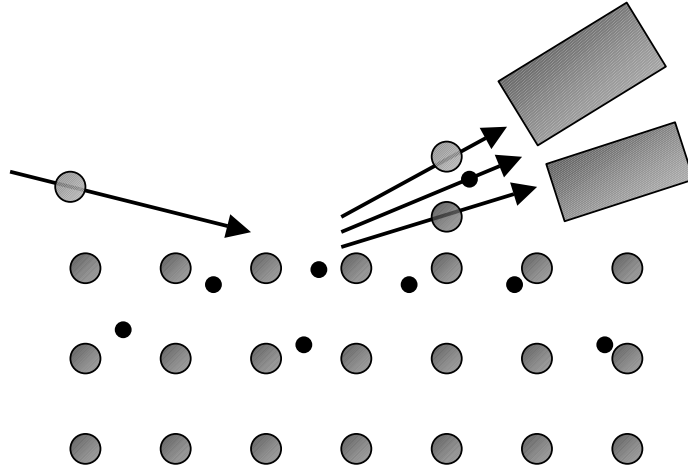


Figure 5.1 Principle of elastic recoil detection analysis (ERDA).

5.1.2 X-Ray Diffraction

For structural investigations of the thin films, x-ray diffraction (XRD) was used. The method is based on incident x-ray beams being diffracted on a material, in a direction and with an intensity determined by the periodicity of the atom planes in a crystalline solid.[3,4] Consider the case where x-rays of wave length λ is incident on a single crystal surface at an angle θ , see Figure 5.2. If the interplanar distance is d , the difference in length traveled by the two rays is $(AC+CB)=2d\sin\theta$. For this to produce a diffraction maxima, the path difference must be an integral number of wavelengths, $n\lambda$. This is the well known Bragg's law for diffraction;

$$2d\sin\theta = n\lambda \quad (5.1)$$

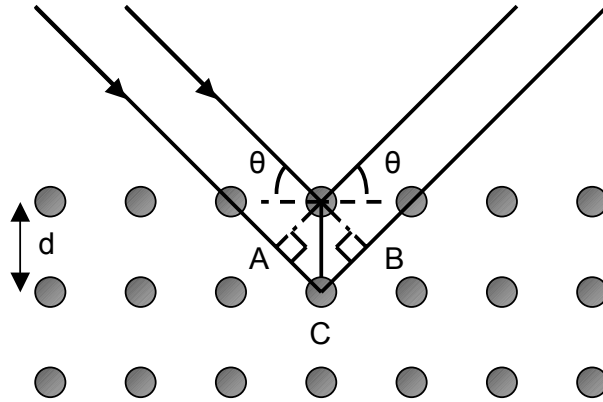


Figure 5.2 X-ray diffraction in a crystalline material.

By knowing λ and measuring θ , d may be determined. Through identification of different sets of crystallographic planes in a material (with different d), phase identification is feasible. Apart from crystal structure (phase), it is also possible to obtain information about grain size (smaller grains result in broader peaks) and stress in the film (through shifted peaks).[3]

Thin film phase analysis was performed with a Siemens D500 diffractometer, operated at an incidence angle of 2° . Cu- K_α radiation was used for the intensity vs 2θ scans, with the generator set to 30 kV and 30 mA.

5.2 Results

Various deposition techniques including chemical vapor deposition (CVD) and physical vapor deposition (PVD) have been used to synthesize alumina thin films: Typically, α -alumina is obtained by CVD at substrate temperatures above 1000°C . [5] The high thermal load then restricts the use of substrate materials, since for example tempering of tool steels occurs already at approximately 550°C . [6] Therefore, much attention has been paid to PVD techniques, which have successively resulted in a significant decrease in α -phase formation temperatures; 690°C (pulsed magnetron sputtering), [7,8] 500 - 650°C (filtered cathodic arc), [9,10] 580°C (plasma assisted CVD), [11] and 280°C (rf sputtering). [12] Correspondingly, the formation of γ -

alumina has been reported at deposition temperatures of ~ 800 °C by CVD,[13] 500-700 °C by plasma assisted CVD,[14] and 350-500 °C by different PVD techniques.[15-17]

One approach to reduce the crystalline growth temperature is to enhance the mobility of surface species through energetic ion bombardment, see for example Ref. 9-11 and 18-19. Hence, the plasma composition and charge state distribution is important since it affects the energy of the impinging ions during film growth, see Equation 1.1 Previously,[9-11,18,19] the effect of a varied substrate bias potential on the phase formation has been investigated. However, neither the charge state distribution nor the IED were studied, the importance of the former being exemplified through a difference of 200 eV ion energy for a singly and triple charged ion at -100 V substrate bias potential, respectively.

In the present study, the effect of ion energy and substrate temperature on the structure and composition of alumina thin films, deposited by cathodic arc, have been investigated. In order to correlate phase formation with synthesis conditions, the previously characterized plasma chemistry and ion energy distributions at synthesis conditions (see Chapter 3.3.2), were included in the analysis.

5.2.1 Composition

It was previously shown that the presence of residual gas in the plasma, may lead to both incorporation thereof in the film [20] and the inhibition of crystalline growth.[21] The result of the here performed ERDA measurements is shown in Figure 5.3, presenting the O/Al fraction as well as the hydrogen content vs substrate temperature, for films grown at -50 and -150 V substrate bias potential, respectively. The hydrogen content in the films is < 0.25 at%. Furthermore, the films contain no additional traces of residual gas, like carbon or nitrogen.

At -50 V substrate bias potential, the O/Al fraction is temperature dependent, see top part of Figure 5.3. Up to 300 °C the films are understoichiometric, while at 500 °C, the value is close to 1.5, corresponding to Al_2O_3 . The oxygen content can be understood by gas adsorption on the substrate surface (see gas inlet close to the substrate in Figure 4.3) with temperature dependent molecule dissociation and diffusion driven incorporation in the film. A similar trend has been observed in a study of O/Mo atomic ratio surface composition as a function of substrate

temperature,[22] where the increasing oxygen content with temperature is explained by diffusion driven incorporation in the film.

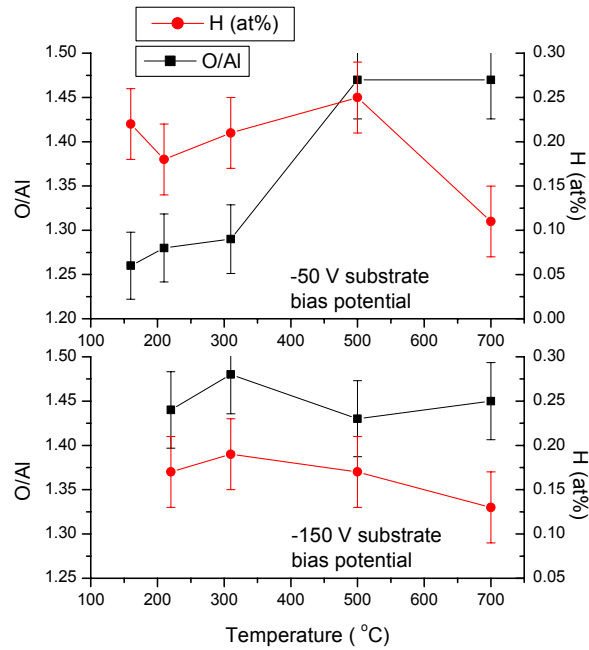


Figure 5.3 Film composition; fraction O/Al and H content (at%) vs substrate temperature as measured with ERDA.

For -150 V substrate bias potential, the films are close to stoichiometric over the entire temperature range, as shown in the lower part of the figure. This can be explained by the increased ion energy (as compared to the -50 V case), supplying the activation energy for dissociation driven diffusion.

5.2.2 Microstructure

An overview of the phase formation in films deposited at different substrate temperatures and substrate bias potentials is presented in Figure 5.4. Four regions can be distinguished; amorphous and weakly ionized films at -50 V substrate bias potential, and at lower substrate potential films containing the γ -phase, the γ -phase with small traces of the α -phase (the intensity of any identified α -peak being less than 10 % of the highest γ -peak), and a mixture between the α - and the γ -phase, at temperatures ≤ 500 °C, 600-700 °C, and 800 °C, respectively.

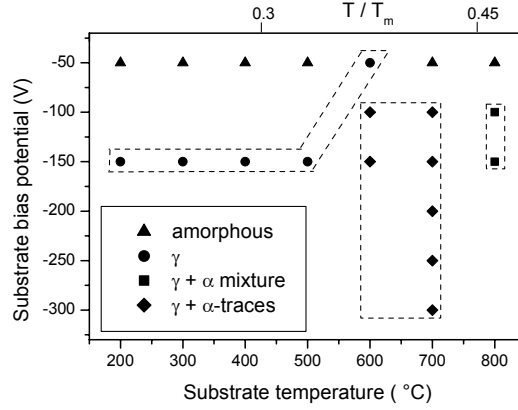


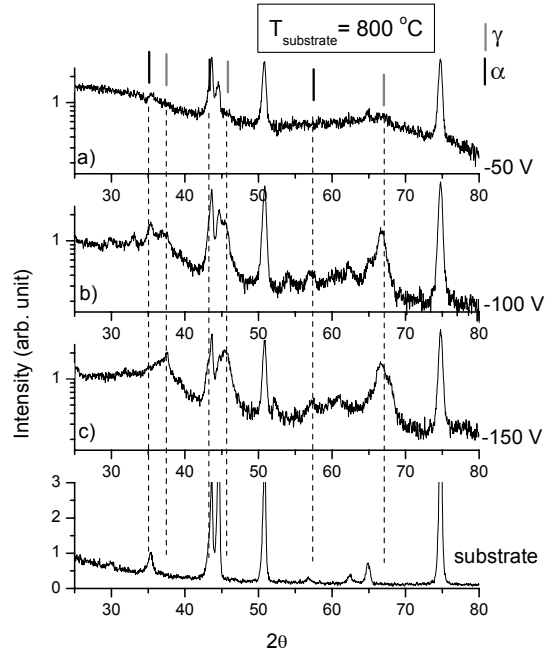
Figure 5.4 Phase formation in films deposited at different substrate temperature and with different substrate bias potential.

The raw data for Figure 5.4 is shown in Figure 5.5-5.8. Inserted in the top scan are the positions of the main peaks of γ - and α -alumina (according to JCPDS [23]). These lines are extended by vertical dotted lines, as a guide to the eye. In order to separate the substrate peaks from the alumina peaks, an XRD scan of a substrate (heated to 700 °C in deposition environment) is also shown.

Previously reported cathodic arc film growth, shows the presence of α -alumina at 800 °C, independent of substrate bias potential used.[9,10] The present investigation therefore included depositions at this temperature, see Figure 5.5.

Figure 5.5 XRD scans for films deposited at 800 °C with a substrate bias potential ranging from -50 to -150 V. Bottom scan is substrate only. The dotted lines show the main peaks of α - and γ -alumina (JCPDS [23]).

At -50 V substrate bias potential (a), the film was close to amorphous, but small traces of both α - and γ -alumina were detected. A lower substrate bias potential, -100 V (b), resulted in a drastic increase



in peak intensity, with an estimated equal phase mixture of α - and γ -alumina. With a substrate potential of -150 V (c), the γ -phase became dominant.

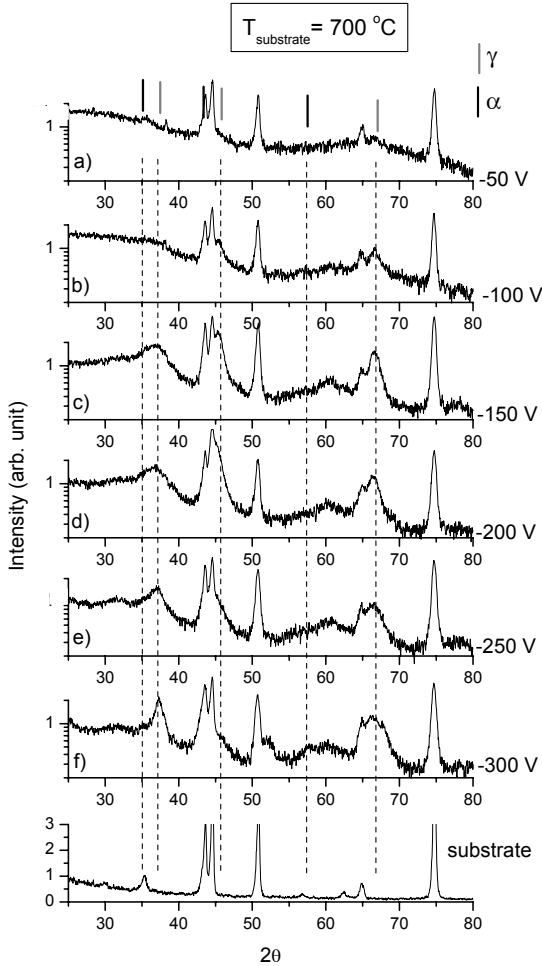


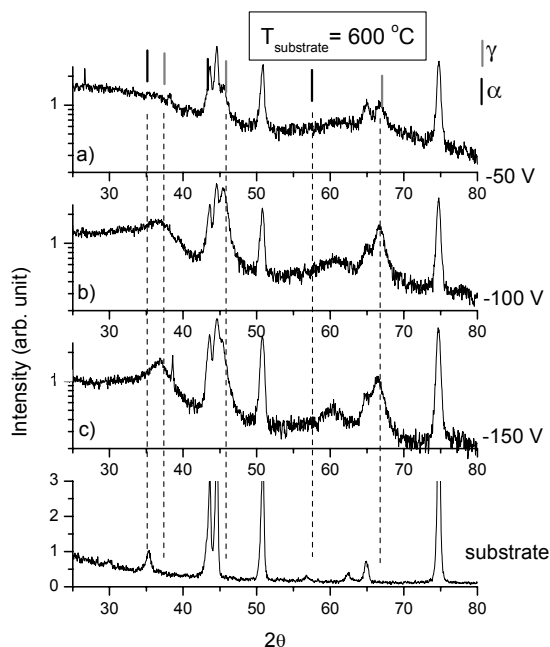
Figure 5.6 XRD scans for films grown at 700 °C with a substrate bias potential ranging from -50 to -300 V. Bottom scan is substrate only. The dotted lines show the main peaks of α - and γ -alumina (JCPDS [23]).

In Figure 5.6, XRD scans for films grown at 700 °C are presented. At -50 V substrate bias potential (a), the film is close to amorphous. At a lower substrate bias potential, the peak intensity increases (b,c), and at -150 V (c) and lower (d-f) the γ -phase is clearly dominating. Traces of the α -phase are also present, with a maximum intensity at -150 V.

For the specific conditions used here, the substrate bias potential required for both γ - and α -alumina formation seems to be ≤ -100 V. Furthermore, the α -phase never dominates the phase mixture. This is not consistent with Ref. 9 and 10 showing a correlation between a lowered substrate bias and an increased content of the α -phase, resulting in α -dominant films. However, a direct comparison is not possible due to differences in the deposition conditions, such as arc

current and magnetic field strength in the plasma filter. The latter is well known to affect plasma composition [24] and ion charge states,[25] which in turn affects the ion energy, see Equation 1.1. Hence, the plasma characterization performed here is essential for progress in understanding structure evolution; one can conclude that for the ion flux specific for the here presented depositions, ion energies in excess of 200 eV (for -50 V substrate bias potential) results in amorphous structure at 700 °C. In contrast, an ion energy distribution ranging from 100 to 550 eV (as exemplified in Figure 3.35 for -100 V substrate bias) is sufficient to enable crystalline growth.

There are several other factors that may be of importance for the phase formation. One is the choice of substrate material, evident from low temperature crystalline depositions using a template.[12,26-27] The films analyzed in Ref. 9 are deposited on vanadium foils, which prior to deposition may react with oxygen and serve as templates. Also the ion flux has been shown to be of significance.[11,18]



Another deposition sequence at 600 °C, showed clearly γ -dominant films for the entire substrate bias potential range, see Figure 5.7, though small traces of α -alumina are present at -100 and -150 V substrate bias potential.

Figure 5.7 XRD scans for films grown at 600 °C with a substrate bias ranging from -50 to -150 V. Bottom scan is substrate only. The dotted lines show the main peaks of α - and γ -alumina (JCPDS [23]).

The high intensity of the γ -peaks motivates a study of this phase at further reduction of the substrate temperature: Figure 5.8a shows phase information for a deposition at 500 °C and -50 V substrate bias potential. The film is amorphous, with small traces of aluminum. (Corresponding depositions at further reduced temperatures, results in completely amorphous films.) The effect of the ion energy is demonstrated in Figure 5.8b-e, where depositions at -150 V substrate bias potential at 200-500 °C show presence of the γ -phase. To our knowledge, the lowest temperature previously reported for the formation of this phase is 290-350 °C.[8] Based on recent reports on the application of γ -phase alumina in metal cutting [28] and steel forming,[29] underlining the (not understood) stability of these thin films, the above reported synthesis route may be of technological interest for the deposition of heat sensitive substrates.

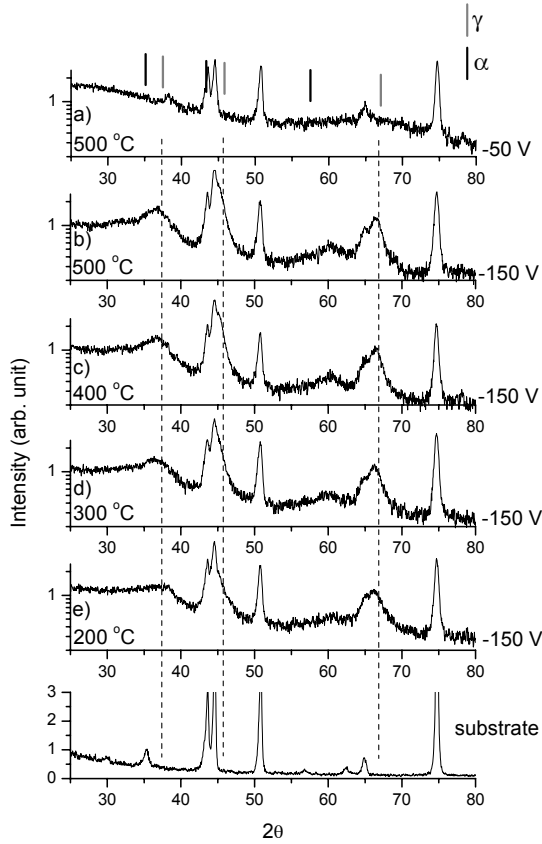


Figure 5.8 XRD scans for films grown at 200 to 500 °C with substrate bias potential of -50 or -150 V. Bottom scan is substrate only. The dotted lines show the main peaks of γ -alumina (JCPDS [23]).

formation upon ion-surface interaction can be expected, see for example Ref. 32, where an increased defect density is shown as the substrate bias potential is decreased from -75 to -150 V. It is well known that defects can serve as nucleation sites for grain growth.[33] Therefore, small sized grains may be expected for the films deposited. Through analysis of the full width at the half maximum of all the non-overlapping peaks in the here presented diffraction data, by Scherrer's formula,[34] the grain size was estimated to be less than 10 nm for both the α - and the γ -phase as well as any mixture thereof. It has previously been shown that the lower surface energy of the γ -phase as compared to the α -phase, thermodynamically stabilizes growth of the γ -phase for nanocrystalline phase formation.[35] The maximum grain size diameter favoring γ -formation, as calculated from Ref. 35 is 12 nm. The here discussed constitution data is therefore consistent with Ref. 35.

According to the structure zone model by Movchan and Demchishin,[30] further developed by Thornton,[31] surface diffusion is initiated at temperatures of $T/T_m > 0.25-0.30$, where T_m is the melting temperature. For α -alumina, this corresponds to 310-420 °C. Correspondingly, bulk diffusion dominates for $T/T_m > 0.45$, which corresponds to $T > 770$ °C. However, the phase analysis presented in this study shows that the ion energy is crucial for the resulting film microstructure. Hence, it is reasonable to assume that the activation energy required for surface diffusion, and hence for the formation of crystalline alumina, is provided by the ion bombardment. As shown in Figure 3.35, the total ion energy distribution extends up to 550 eV at -100 V substrate bias potential. At these energies, defect

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6. DFT based methods for thin film growth related studies

This chapter provides a general introduction to the theoretical investigations presented in this work, including a short summary of Density Functional Theory.

6.1 Introduction to the field

An increased fundamental understanding of thin film growth is gained when experimental investigations are performed in parallel with theoretical calculations or simulations. The latter two concepts will here be separated; a calculation gives properties of one specific state of a system, while a simulation is a sequence of calculations that describes the transformation of the system from an initial state to a final state. Theoretical studies can be very useful: While experiments often describe macroscopic properties of the final state of a system, theory based on quantum mechanics can be used to describe fast processes on the fs scale occurring at the atomic level during a transformation. Additionally, experiments that are difficult or impossible to carry out under, for example, extremes of temperature, are feasible with simulations. However, the two approaches should be considered complementary, where theory can serve both as prediction and confirmation of experimental results.

The major distinction in the field of theory, is between classical calculations / simulations and those based on quantum mechanics. The main

advantage of the former is the possibility to simulate large systems (thousands of atoms), while the major drawback are the challenges associated with identifying suitable potentials describing the atomic/molecular interaction. Due to large computational requirement of CPU time, quantum mechanical calculations are often limited to systems of ~ 100 atoms. However, instead of model potentials, the electronic structure is explicitly treated, and therefore many-body forces, electronic polarization and bond-breaking and forming events can be described to within the accuracy of the electronic structure representation.

In this work, quantum mechanical calculations and simulations within the framework of Density Functional Theory (DFT) are being presented. Before going into details of the method chosen, a short theoretical background is given: The quantum mechanical equation describing a system is the Schrödinger equation

$$H \Psi = E \Psi \quad (6.1)$$

where H is the Hamilton operator connected to the kinetic and potential energy of all particles, E is the total energy of the system (conserved if H is conserved) and Ψ is the wave function describing the system.

A wave function for an N -electron system contains $3N$ coordinates (if excluding spin), resulting in an equation which for $N > 1$ is impossible to solve. One must therefore rely on different approximation methods, or expand the theories of electronic systems, as discussed below.

6.2 Density Functional Theory

The main formal complexity encountered when treating a material quantum mechanically, is the correlations between the particles. The position and motion are correlated because the particles interact with each other and exert forces upon each other as they move. Additionally, there is the complex force that devolves from the Pauli exclusion principle governing electrons. This force is referred to as the exchange force.

An important advance in the calculation of the energy of collections of atoms and the forces on each atom has been made through DFT, see for example Refs. 1-2. The basis is the proof by Hohenberg and Kohn,[3] stating that the ground-state

electronic energy is determined completely by the electron density ρ , meaning that there exists a one-to-one correspondence between the electron density of a system and its energy. Thus, a mean field theory can be applied [4] where the Schrödinger equation with $3N$ variables is reduced to an equation involving the electron density ρ of only three variables, the Kohn-Sham equation.[4] For this approximation, Kohn was awarded the Nobel Prize in chemistry 1998. An expression for the DFT energy E can consequently be written

$$E[\rho] = T_s[\rho] + E_{es}[\rho] + E_{xc}[\rho] + E_{ext}[\rho] \quad (6.2)$$

where T_s is the kinetic energy of non-interacting electrons, E_{es} is the electrostatic energy, E_{xc} is the exchange correlation energy, and E_{ext} is the energy due to an external potential. The terms are known and can be calculated, with the exception of E_{xc} which must be approximated.

The simplest and traditional approximation of E_{xc} is referred to as the Local Density Approximation (LDA),[4] where it is assumed that the electron density locally can be treated as a uniform electron gas. LDA can be considered as the first term in a gradient expansion, valid in the limit of slowly varying electron density. However, the approximation has in general been successful in predicting physical properties of systems. Though LDA is and has been used extensively, the approximation tends to overestimate binding energies. Therefore, corrections to the LDA have been developed that are dependent on the gradient of the density, generally referred to as *gradient corrected* or Generalized Gradient Approximation (GGA).[5] This approximation has little influence on local properties such as bond lengths, but usually leads to more accurate bond energies.

For computational efficiency the core and valence electrons are treated separately. This is justified by the observation that the core electrons are rather unaffected by the chemical environment of the atom.[6] So-called pseudopotentials are used to represent the core electrons, meaning that these are modeled by a suitable function specific for the atomic species, and only the valence electrons are treated explicitly. The wave functions for these electrons are expanded in terms of a discrete set of plane waves (according to Bloch's theorem [7]) with kinetic energies up to some specified cutoff energy.

Despite various approximations, usage of the theory described above would not be possible without powerful software packages, of which several options exist

[8]. In this thesis, all presented calculations and simulations are performed using the program package CASTEP from Accelrys, Inc.[9]

6.2.1 *Ab initio* (0 K) calculations

Quantum mechanical calculations are usually denoted *ab initio*, originating from Latin “from the beginning”. It refers to the origin of theoretical derivations only, excluding empirical input into the equations describing the system. To perform calculations one needs to start with a model of the system under investigation. The model must be designed after the method used, in order to achieve accurate results without the calculations being too time consuming.

Generally, periodical boundary conditions are used for the calculations, meaning that a cell model is repeated periodically in three dimensions. In the case of surface studies, repeated layers of infinite slabs are thereby formed. One of the requirements is that the thickness of the slab, as well as the vacuum layer in between the slabs, are large enough to facilitate a negligible interaction between the individual cell surfaces. Furthermore, in for example adsorption studies, the width of the cell is of importance in order to avoid interaction between adsorbates in adjacent cells. Test calculations prior to investigations are therefore of importance, usually involving change in parameters and approximations until convergence in, for example, energy is obtained.

The specific approximations used in the calculations within the present work were, for the exchange correlation, the LDA (LSDA) functionals as developed by Perdew-Zunger [10] and the GGA (GGS) functionals as developed by Perdew-Wang.[11] The valence electrons were represented by a plane-wave expansion up to a cutoff energy of 260 eV, where the k-points used for the plane-waves were generated according to Monkhorst-Pack,[12] producing a uniform mesh of points in reciprocal space. Furthermore, electron-ion interaction was described by an ultrasoft pseudopotential in the Kleinmann-Bylander form.[13]

Calculations on static systems (0 K) can provide a wealth of information, both structural (equilibrium) information, and a variety of electronic properties. Examples of the latter are charge density (bond populations), band structure, and optical properties. When investigating, for example, adsorption reactions on a surface, these are dependent on the temperature of the system. Nevertheless, 0 K calculations are

widely used to investigate differences in adsorption energetics, which is assumed to be preserved with increasing temperature.[14] Studies of dynamical behavior at temperatures above 0 K demand other methods, such as molecular dynamics simulations.

6.2.2 *Ab initio* Molecular Dynamics ($T > 0$ K)

Computer simulations may generate information at the atomic level, and this very detailed information can be related to macroscopic parameters, such as pressure and temperature. The thermodynamic state of a system can be defined by a set of these parameters, and depending on simulation conditions, a specific set is kept constant during a simulation. In most common use is the so-called microcanonical ensemble (with a fixed number of atoms N_a , fixed volume V , and fixed total energy E).[15]

The classical equation governing the time evolution of a system is Newton's second law, which can be written as

$$-\frac{dV}{dr} = m \frac{d^2 r}{dt^2}$$

$$F = ma \tag{6.3}$$

where V , r , F , m , and a equals the potential, position vector, force, mass and acceleration, respectively. In a molecular dynamics (MD) simulation, a succession of states is generated from this equation, in accordance with the chosen ensemble. A corresponding *ab initio* MD is based on the same principle, but the system behavior is commonly studied using forces calculated from the Kohn-Sham equation.[6] It is a time-consuming method, though very informative through the possibility of computation of both equilibrium thermodynamic and dynamical properties as well as atomic level information explicitly including electronic structure.

In the here presented work, the simulations were performed through *ab initio* MD, solving the Newtonian equations using the velocity Verlet propagator.[16] Requirements on the model are similar as described in Chapter 6.2.1, with periodical boundary conditions. All simulations were performed in the microcanonical ensemble, in time steps of 1 fs at a temperature of 330 K. The cutoff energy for the plane waves were between 260 and 300 eV, with 1-4 generated k-points.[12] LDA functionals (Perdew-Wang)[11] were used for the exchange correlation approximation, while

ultrasoft pseudopotentials (Kleinman-Bylander)[13] were used for electron-ion interaction.

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7. Results of theoretical investigations

The main focus of the research presented here is the influence of ion energy/plasma chemistry on the film composition and microstructure. The strategy to contribute towards understanding has been to carry out thin film growth related theoretical studies, investigating ion-surface interactions prior to collision, ion / atom adsorption, surface migration and local structural as well as compositional changes accompanying surface bombardment.

7.1 Models

7.1.1 Alumina, α -Al₂O₃

α -Al₂O₃ has served as a prototype for understanding metal oxides in numerous experimental and theoretical investigations. Some of these investigations suggest that the relaxed crystal structure with a single terminating Al layer (0001) results in the most stable *clean* surface, shown theoretically in for example Ref. 1-4, and also experimentally in Ref. 5-6. However, the termination is still a matter of debate; Calculations of Barytrev et al. suggest that oxygen termination is stable by exposure at an oxygen pressure of ~100 kPa.[7] Renaud reported O-terminated structures that were prepared by heating in an oxygen rich atmospheres,[8] and Jaeger[9] suggested the same termination based on experimental investigations on ultra thin films of

alumina. Toofan and Watson found both O and Al terminated domains in 2:1 ratio[10] using low energy electron diffraction (LEED) analysis, a mixture which was also observed by Ahn.[11] The discrepancy between different theoretical predictions and experimental results may be explained by the presence of hydrogen: The O-terminated surface is expected to be unstable due to the non-zero dipole moment resulting from the stacking sequence, O-Al-Al, of the crystal. However, adding one hydrogen per unit cell drastically lowers the free energy,[12] and therefore stabilizes the O-terminated surface. Calculations show that a hydrated (0001) surface is oxygen terminated.[13,14] Hydrogen stemming from the residual gas may be present during thin film growth,[15] and detailed experimental investigations have detected H chemisorbed to the surface[11,14,16], as well as H that was incorporated during thin film growth.[17,18] Therefore, an O-terminated α -Al₂O₃ surface has been chosen for the present α -Al₂O₃ studies.

The test calculations prior to the investigations involved calculations of the adsorption energy of Al⁺ in its bulk position on an α -Al₂O₃ (0001) surface, and the cell was enlarged until convergence in adsorption energy (< 4 % difference) was obtained. The size of the slab in the x-, y-, and z-direction, the vacuum layer, as well as the number of movable atoms, were then varied. The resulting O-terminated slab contains three layers of oxygen (O-Al-Al-O-Al-Al-O-Al-Al), which is a thickness reported to be well suited for surface energy studies.[19,20] The hexagonal super-cell size is 9.52, 9.52 and 12.99 Å (with a vacuum depth of 7.4 Å), which is consistent with literature to be large enough to ignore mutual influence of the surfaces.[5,19,20] A topview of the resulting supercell is shown in Figure 7.1.

Additional test calculations were performed prior to the MD simulations: Different collision sites, as well as different collision energies, were tested, in order to find conditions where the cell depth was large enough and where collision effects from adjacent cells could be neglected. Hence, an upper limit of 3.5 eV was identified for collisions where an ion was positioned directly above a surface atom. Furthermore, the reproducibility within the present investigation was tested, which resulted in no observable variations (the same final geometry of the system).

The 0 K calculation procedure was divided in two steps; a so-called geometry optimization followed by a single-point-energy calculation. The former relaxes the structure to the geometry corresponding to minimum total energy, and the latter is a

recalculation of the total energy, using a more accurate approximation. The lowest atomic layers are fixed during geometry optimization to simulate bulk conditions, which does not significantly influence the results. In the present studies, the LDA/LSDA method was used for the geometry optimization, as well as for the MD simulations, since it is well known to result in rather accurately described local properties such as bond lengths (i.e. structure). Furthermore, the GGA/GGS method was used for the single-point-energy calculations.

The theoretical investigations on the α -Al₂O₃ surface presented here, constitute various forms of ion-surface interaction. In common for the investigations is the aim for a deeper understanding of microstructure evolution during film growth, especially for alumina. The sequence of an ion approaching and being incorporated in the top surface layers, is divided into separate studies; ion-surface interaction prior to adsorption, adsorption, surface migration and local structural changes induced by ion bombardment.

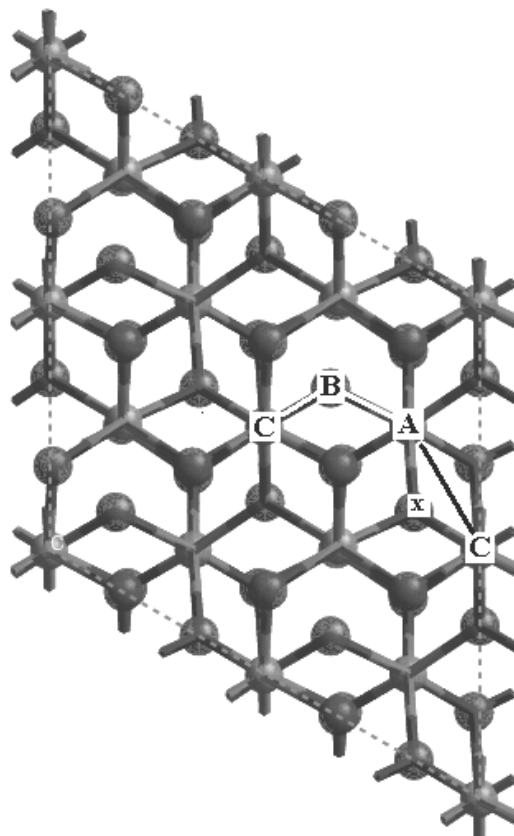


Figure 7.1 Top view of simulation model of an α -Al₂O₃ (0001) surface. Investigations have included adsorption (at site A, B, and C), migration (inserted lines), and surface bombardment (at site x and C).

7.1.2 Gibbsite, $\text{Al}(\text{OH})_3$

The study of compositional evolution has here been focused on the incorporation of residual gas (mainly H_2O). Gibbsite, or aluminum hydroxide, was chosen for the theoretical investigation. It can be described as hydrated $\alpha\text{-Al}_2\text{O}_3$ with monoclinic crystal structure.[21] (The basic structure of corundum is identical to gibbsite except the hydroxides are replaced by oxygen.)

Test calculations performed prior to the MD simulation of an $\alpha\text{-Al}_2\text{O}_3$ surface were assumed to be valid also for the gibbsite surface, considering a larger cell size and an increased number of atoms used in the gibbsite supercell. The hydrogen terminated (0001) surface was chosen for the study, in accordance with the experimentally observed preferential cleavage surface.[21]

It has previously been reported that hydrogen incorporation is decisive for the film composition as well as the microstructure evolution in strontium titanate thin films.[22] Furthermore, the amount of hydrogen in the films was strongly affected by the growth temperature, which reflects the importance of the energy supplied. In addition to substrate heating the energy can be supplied also through particle bombardment, which is the topic of the theoretical investigation performed here. The goal is to contribute towards a fundamental understanding as well as to investigate possible ways to affect the hydrogen incorporation, through MD simulations of ion bombardment of the gibbsite surface.

7.2 Studies related to $\alpha\text{-Al}_2\text{O}_3$ thin film microstructure

7.2.1 Ion-surface interaction prior to adsorption

Plasma production by cathodic arc results in ions moving with a directed velocity towards the substrate surface. MD simulations (at 330 K) have here been performed to investigate interaction prior to the ion-surface collision: An Al^{1+} ion ($\text{Al}_{\text{in}}^{1+}$) was initially positioned approximately 2 Å above the (0001) surface at position $\mathbf{x}$, see Figure 7.1. In a subsequent simulation, the trajectory of the ion was studied as it approached the surface, presented in Figure 7.2. The figure is divided in two parts, the

top presenting the xz-view of the investigated surface region, and the bottom the corresponding yz-view. The trajectories for four different initial energies (0.9 eV (■), 3.5 eV (▲), 14.0 eV (▼) and 31.5 eV (►)) are shown in time steps of 5 fs, until ion-surface collision occurs.

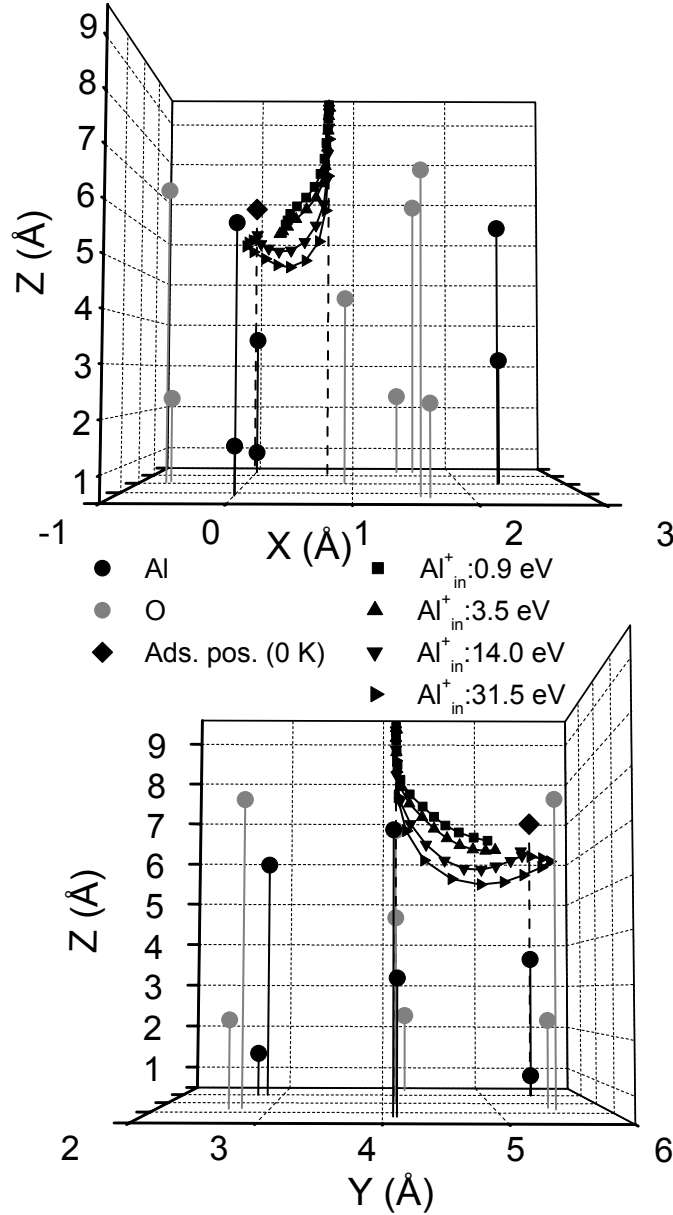


Figure 7.2 MD trajectories of an Al^{1+} ion approaching the (0001) surface at different initial energies, as well as the calculated (at 0 K) equilibrium position of an Al^{1+} adsorbate.

Additionally, Figure 7.2 also shows the relaxed equilibrium position ($\blacklozenge$) corresponding to a local potential minimum of an Al^{1+} adsorbate, obtained in DFT calculations at 0 K (see adsorption study below). As can be seen, independent of energy, the ion trajectories in the vicinity of the potential minimum deviates towards this equilibrium position. It is therefore evident that ion-surface interactions promote adsorption at local surface potential minima.

7.2.2 Adsorption

Surface reactivity and adsorption studies have earlier been reported for $\alpha\text{-Al}_2\text{O}_3$ (0001): For O-terminated surfaces, Kruse et al. reported Nb interaction with the oxide,[23] Bogicevic et al. studied metal adsorption (1/3-4 ML) on ultrathin films,[24] and Lodziana calculated the interaction of Cu and Pd (1 ML) with the surface.[25] These latter investigations show that, in comparison to Al terminated surfaces, the interaction with O-terminated surfaces is stronger,[25] more ionic (especially at low coverage),[24,25] and there are also indications of preferred adsorption sites.[24]

No systematic adsorption study of Al^{1+} , Al^{2+} , Al^{3+} , and O^+ on an O-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface is available in the literature. Here, DFT calculations have been used for this purpose. The surface reactivity will most probably affect the incorporation site, and may therefore influence the resulting structure evolution. The effect of surface site and charge of the metal adsorbates on the adsorption energy, as well as the nature of the adsorbate-surface bonding situation, have therefore been investigated. The adsorption of O^+ , the most abundant non-metal ion detected in an Al arc plasma in an oxygen environment, has also been included.[26] The ions chosen have been observed in plasma chemistry measurements of an Al arc plasma in an oxygen environment, in the presence of magnetic fields [26] as well as without magnetic fields.[15]

Three differently located adsorption sites were chosen on the surface, see Figure 7.1. The sites were; A – above an Al atom in the 3rd atomic layer, B – above an O atom in the 4th layer, and C – above an Al atom in the 2nd layer. Site A corresponds to the bulk position of an Al ion, whereas B and C interrupt the crystalline sequence of positions. The adsorbates were initially positioned at these sites (approximately 1 Å over the surface), and the subsequent geometry optimization resulted in the structure

for which the total energy was calculated. The adsorption energies, E_{ads} , of the different ions were calculated using

$$E_{ads} = E_{a+s} - (E_a + E_s) \quad (7.1)$$

where E_a is the energy of the free ion (with charge $+q$), E_s is the total energy of the relaxed surface without adsorbate (with charge $-q$) and E_{a+s} is the total energy of the relaxed surface with adsorbate.

A: Metal adsorption

Charge dependence

The influence of the charge of the adsorbate (also referred to as charge state) on the adsorption behavior, was studied by comparing adsorption of different ions at identical surface sites. As can be seen in Table 7.1, the initial charge of all Al ions was found to clearly affect the magnitude of the adsorption energy, E_{ads} , at all surface sites studied (A, B, or C).

	Al ¹⁺		Al ²⁺		Al ³⁺	
	E_{ads} (eV)	C_f	E_{ads} (eV)	C_f	E_{ads} (eV)	C_f
A	-20.98	1.96	-36.70	1.95	-(x+4.67)	1.96
B	-19.19	1.95	-34.71	1.93	-(x+4.21)	1.90
C	-15.42	1.89	-30.70	1.88	-(x)	1.88

Table 7.1 Adsorption energy (E_{ads}) and final charge (C_f) of the Al ions at the adsorption sites.

Since ultrasoft pseudopotential functions were used in the calculations, adsorption energies could only be calculated for Al¹⁺ and Al²⁺ ions. E_{ads} were, for all surface sites, found to be strongly exothermic, and was for Al²⁺ approximately 16 eV larger than for Al¹⁺. It is reasonable to assume that the main contribution to this difference is the *initial potential energy difference*. Additionally, as the free ion moves towards the surface, several subprocesses will occur (e.g. subsequent charge transfer and relaxation) that generally results in a decrease in total energy to an equilibrium value. Turning to Table 7.1, it can be seen that the final charge of the adsorbates (at identical adsorption sites) are similar. From this one can conclude that the charge transfer between the adsorbate and the surface is strongly dependent on charge of the adsorbate. The first and second ionization energies of Al is 6 and 18.8 eV,

respectively.[27] Furthermore, one additional charge added to the surface prior to adsorption results in a calculated increase in total energy of 2.9 eV. Close to one electron is transferred to the surface during Al^{1+} adsorption, whereby an adsorption energy can be estimated from the difference between the ionization energy of Al^{1+} , and the energy increase associated with the additional charging of the surface, $(18.8 - 2.9)$ 15.9 eV. The calculated difference in adsorption energy between Al^{1+} and Al^{2+} is 15.3 to 15.7 eV, which in Figure 7.3 can be compared to the inserted bars of 15.9 eV.

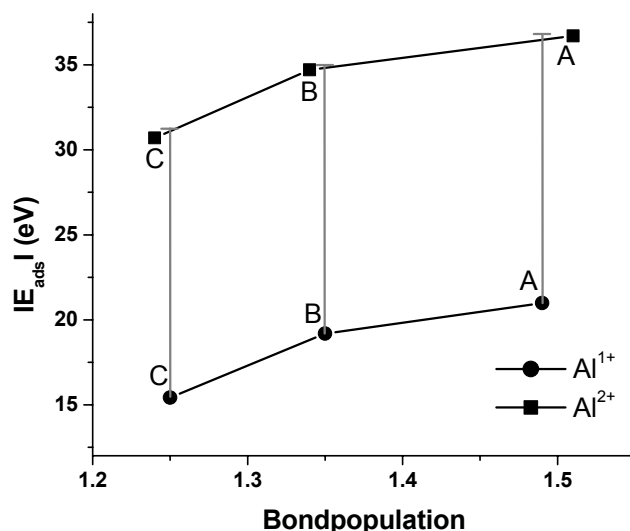


Figure 7.3: Adsorption energy ($|E_{\text{ads}}|$) versus bond population for Al^{1+} and Al^{2+} ions adsorbed on the surface sites A, B and C.

Other contributions to the adsorption energy can be discussed in terms of surface reconstructions, and adsorbate-surface bonding. As can be seen in Table 7.2, the calculations for both Al^{1+} and Al^{2+} resulted in the formation of three Al-O bonds between adsorbate and surface (for all of the three sites studied). The bond population is correlated to the electron density in the bonding region between two atoms, indicating the contribution of covalent bonding to the overall bonding character. No significant differences in bond lengths and bond populations for the different ions at an identical site can be detected. In addition, the large similarity in final charge and bond lengths for the adsorbates (at identical surface sites; see Table 7.1), indicate no significant difference in the ionic contribution to the overall bonding character either.

7. Results of theoretical investigations

These observations underline the suggested role of the difference in initial potential energy for the adsorption energy differences discussed.

	Atom	Al ¹⁺		Al ²⁺		Al ³⁺	
		Pop.	Bondl. (Å)	Pop.	Bondl. (Å)	Pop.	Bondl. (Å)
A	O ₃₆	0.50	1.67	0.50	1.67	0.50	1.67
	O ₃₀	0.50	1.67	0.50	1.67	0.50	1.67
	O ₂₆	0.49	1.68	0.51	1.67	0.50	1.67
B	O ₂₈	0.47	1.63	0.46	1.64	0.44	1.68
	O ₃₂	0.47	1.65	0.47	1.67	0.45	1.70
	O ₃₆	0.41	1.73	0.41	1.75	0.19	2.24
	O ₃₄					0.47	1.72
C	O ₂₅	0.42	1.72	0.42	1.72	0.42	1.72
	O ₃₆	0.42	1.72	0.41	1.72	0.41	1.72
	O ₃₂	0.41	1.72	0.41	1.72	0.42	1.72

Table 7.2 Bond lengths and bond populations between the Al adsorbates and the adsorbate-binding surface atoms (denoted O_{nr}).

The total energy of the final structure (surface + adsorbate) was found to be independent of the initial charge of the adsorbate, with the exception of Al³⁺ adsorbing on the nonequilibrium sites B and C, respectively (see Table 7.3).

	Al ¹⁺	Al ²⁺	Al ³⁺
	E _t (eV)	E _t (eV)	E _t (eV)
A	0.19	0	0.11
B	1.92	1.99	0.57
C	5.69	6.0	4.78

Table 7.3: Total energy (E_t) of the resulting configurations (surface+adsorbate) relative to the structure of lowest energy (Al²⁺ adsorbed on site A).

This may be due to the increased number of nearest neighbors (around B and C) accompanying the charge transfer between adsorbate and surface, with resulting larger atomic displacements detected (more accentuated for site B). This is indicated in Table 7.2 (site B), where a clear difference in bond length and population for Al³⁺ and the other two adsorbates can be seen.

Site dependence

Significant energy differences are found when comparing adsorption of one specific ion at different adsorption sites, see Table 7.1. When studying the site dependence for Al^{1+} , the adsorption energy is calculated to -21.0, -19.2 and -15.4 eV for site A (equilibrium site, above Al), B (nonequilibrium site, above O) and C (nonequilibrium site, above Al), respectively. The ions Al^{2+} and Al^{3+} show the same trend. This may be understood by analyzing the bonding situation between the adsorbate and its closest neighbors. It is well known that the overall bond strength is sensitive to covalent, ionic and metallic contributions. Here we investigate the site dependence of a) the bond population and b) the final charge state of the adsorbate, as a measure for the covalent and ionic contribution to the overall bond strength, respectively. It has earlier been shown that the magnitude of the bond populations correlates with the bond strength in various bulk crystals (including oxides).[28] The bond populations given in Table 7.2 show a decrease in magnitude when going from site A to site C (via site B). The adsorption energies for Al^{1+} and Al^{2+} versus the sum of the populations in the bonds between the adsorbate and its nearest neighbors is plotted in Figure 7.3. As expected, an increase in bond population corresponds to an increase in adsorption energy, $|E_{ads}|$. The same trend is detected for the relative energies of Al^{3+} , though not as pronounced.

The ionic contribution to the overall bond strength is indicated in Table 7.1. In addition to the bond lengths, a comparison between the different relative ionic (and covalent) bond strengths can be made by looking at the final charge of the adsorbates. Moreover, the correlation between the adsorption energy for Al^{1+} and Al^{2+} , and the final charge of the adsorbates is shown in Figure 7.4. The lattice site A (with the largest adsorption energies) do correspond to the highest final adsorbate charges. Site C (with the smallest adsorption energies) has the lowest charges, and the result for site B is in between A and C. When comparing the results presented in Figure 7.4 and Table 7.2, a correspondence between an increased bond length, a decreased charge, and a decrease in ionic bond strength can hence be found when going from surface site A to C. The ordering of the surface adsorption sites on an adsorption energy scale may therefore be explained by an indicated change in bond strength for *both* the ionic and covalent part. It should furthermore be noted that the ionic interaction is stronger at the surface as compared to in the bulk. This is evident from the charges of the

adsorbates being close to 1.9 (Table 7.1) and the charges of Al in the middle of the slab being close to 1.7.

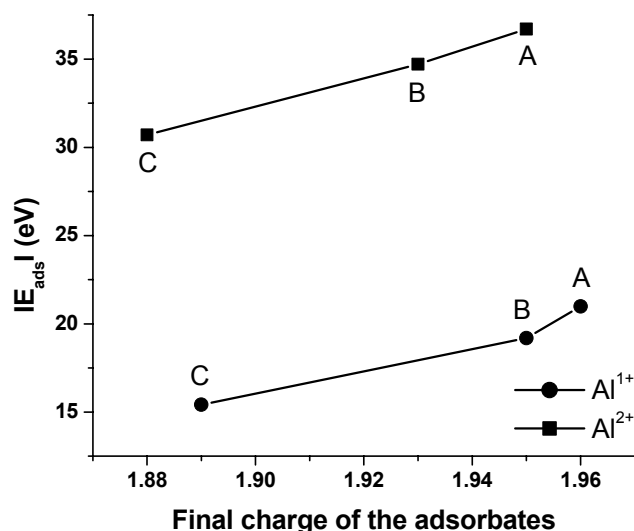


Figure 7.4 Adsorption energy ($|E_{ads}|$) versus final adsorbate charges for Al^{1+} and Al^{2+} ions adsorbed on the surface sites A, B and C.

A comparison between the adsorption energy of different $\alpha-Al_2O_3$ (0001) sites could possibly give information about preferred surface sites during thin film growth, and consequently a clue to evolving crystal structures. All ions show strong exothermic reactions when adsorbed to different surface sites. Site A corresponds to a bulk equilibrium position of an Al ion and results in the highest adsorption energies (absolute values) of the three sites studied. Site B, though not a bulk position, results in a lower adsorption energy for the Al^{1+} and Al^{2+} ions, but for Al^{3+} adsorption site B shows similar value (difference of 0.46 eV) as for site A (Table 7.1). This similarity between A and B surface sites could indicate that, in the presence of Al^{3+} ions, it is likely that an amorphous material will evolve during film growth since the crystal bulk sites are then not energetically preferred.

B: Nonmetal adsorption

The oxygen ionic species O^+ is often the most abundant non-metal ionic species in an Al/oxygen arc plasma.[26] By applying the same research strategy as for evaluating the strong surface site dependence of the Al ions, the adsorption energy of

O^+ at the different sites (A, B, C) were found to show similar values (ranging from -16.9 to -17.5 eV), see Table 7.4.

	O^{1+}				
	E_{ads} (eV)	C_f	Atom	Pop.	Bondl. (Å)
A	-17.50	0.12	O ₃₀	0.32	1.37
			O ₂₆	0.24	1.47
			O ₃₆	0.00	2.19
B	-16.93	0.11	O ₂₉	0.30	1.39
			O ₃₇	0.29	1.46
C	-17.20	-0.02	O ₃₆	0.11	1.58
			O ₂₅	0.09	1.59
			O ₃₂	0.08	1.62

Table 7.4 Adsorption energy (E_{ads}) and final charge (C_f) of the O^+ adsorbate, together with the bond populations and bond lengths between the adsorbate and the adsorbate-binding surface atoms (denoted O_{nr}).

There is about one electron being transferred from the adsorbate to the surface. The initial charge of the adsorbate is +1, and the final ones are 0.12, 0.11 and -0.02 for site A, B and C, respectively. A comparison of the bond populations in Table 7.4 do also show lower total values for site C. One plausible contribution to these differences is the adsorption-induced surface geometry changes: **Site A and B:** Adsorption at these sites resulted in atomic displacements of the nearest neighbors in the top O layer (comparable to results of Al^{1+} and Al^{2+}). The second atomic layer (first Al layer) showed hardly any geometrical changes. The resulting adsorbate-surface distance were larger as compared to the Al adsorbates. **Site C:** The adsorption resulted in a somewhat different final geometrical structure, with more changes in surface geometry than found both at site A and B, and for the Al adsorbates at site C. Especially the three closest binding atoms to the adsorbate showed an outward relaxation, though the resulting distance of the O adsorbate above the main part of the surface were comparable to the results of the Al adsorbates. The first Al layer was also influenced geometrically.

All three adsorption sites interrupt the crystalline atom sequence when O^+ is adsorbed, and all sites studied result in exothermic adsorption reactions. The adsorption of O^+ on an O-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface with adsorption energies

within 3.8 eV from those of Al^{1+} , and at site C even 1.78 eV lower as compared to Al^{1+} , may indicate amorphous growth for kinetically limited systems. Alumina synthesis by physical vapor deposition is known to result in the formation of an amorphous structure at substrate temperatures $\leq 250^\circ\text{C}$. [29] It is therefore suggested that the here presented findings may at least in part serve as an explanation for the reported experiments.

In summary, the adsorption processes of Al^{1+} , Al^{2+} , Al^{3+} and O^+ on an O terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface have here been investigated. All adsorption reactions were found to be exothermic, and adsorption on the equilibrium (bulk) lattice position resulted in the most preferred adsorption situation. Numerically similar adsorption energies for Al^{3+} adsorbed on different surface sites indicates that amorphous film growth may be likely to occur with Al^{3+} ions as film-forming material. The O^+ ions showed less dependence of adsorption energy on surface site, with energies similar to those calculated for Al^+ adsorption. These results may explain the experimentally observed formation of amorphous structures during kinetically limited alumina thin film growth.

7.2.3 Surface migration

Thin films of $\alpha\text{-Al}_2\text{O}_3$ can be achieved for example if energy is supplied through growth at temperatures above 800°C [30], with a substrate bias of -50 V [31] and -200 V [30] at temperatures around 650°C , as well as through (local) epitaxy. [32] The supplied energy affects the structure evolution of the material through the ability of the atoms to diffuse, at the surface and in the bulk. To gain fundamental understanding of the evolving structure during film growth, it is essential to theoretically study diffusion/migration. Several investigations concerning alumina diffusion can be found in literature, as exemplified in Ref. 33-35: Belonoshko et al. calculated the temperature dependent diffusivity of hydrogen in bulk alumina [33], and Harding et al. simulated grain boundary diffusion in ceramics, including $\alpha\text{-Al}_2\text{O}_3$. [34] A theoretical study of Pd migration on the (0001) surface were performed by Lodziana et al, indicating an atom mobility high enough for diffusion at room temperature. [35]

In the study presented above (Chapter 7.2.2), the adsorption of different Al and O ions on an $\alpha\text{-Al}_2\text{O}_3$ (0001) surface was investigated. If extending the study to

also include neutral Al, the results will also be relevant for plasma based growth techniques with a lower degree of ionization (for example magnetron sputtering).[36] Table 7.5 shows the adsorption energies at different sites for neutral Al.

Site	Ads. energy: Al (eV)
A	-10.08
B	-9.7
C	-2.82

Table 7.5 Adsorption energy of an Al atom at the sites investigated

Site A, corresponding to the bulk (equilibrium) position of Al, results in the largest adsorption energy, whereas B and C (interrupting the crystalline sequence of positions) result in less exotherm adsorption reactions. This trend is in accordance with the results of the metal ions, showing a strong site dependence. *All* adsorption reactions/sites investigated resulted in exotherm reactions, indicating *local* minima in surface potential at these sites. The difference in magnitude of the adsorption energies indicates that there are barriers for surface migration between the different sites, otherwise the geometry optimization would have resulted in the same final location of the adsorbates. However, no corresponding surface migration data for the film forming species of alumina are available. This information is needed, since the height of these barriers strongly affects the evolving surface structure, by impeding the adsorbate movement on the surface. Hence, migration studies have been performed here, with Al^{1+} (the most abundant metal ion in an Al cathodic arc plasma at elevated oxygen pressures [15]) as the adsorbed species.

Ab initio calculations of migration barriers on a surface are carried out in two major steps in order to locate an optimized transition state geometry: First, the potential path between two adsorption sites of interest are calculated, by moving the adsorbate in steps on the axis intersecting both sites. Each step includes a geometry optimization of the surface, while the adsorbate is fixed. The maximum obtained in the potential curve corresponds to the projected (in xy-plane) transition state. Secondly, a similar procedure is performed to identify the real transition state position: From the projected state, the adsorbate is moved in steps perpendicular to the intersecting axis. A minimum in this second potential curve corresponds to the located transition state, with a geometry onto which further calculations can be

performed. The migration barriers are calculated by taking the difference in energy of the transition state and the adsorption sites investigated.

After an ion-surface collision, the adsorbate may stay at the collision site or start to migrate on the surface. If, and to what extent, depends on the presence and magnitude of migration barriers. The migration paths investigated in the present paper, are the shortest distances between adsorption sites A, B, and C, respectively (see Figure 7.1). A potential energy change, following a surface migration from one adsorption site to the neighboring one, is shown in Figure 7.5. These potential energy vs distance curves correspond to a projection of the transition states on the xy-plane. The final transition states are located at the energy minima in Figure 7.6.

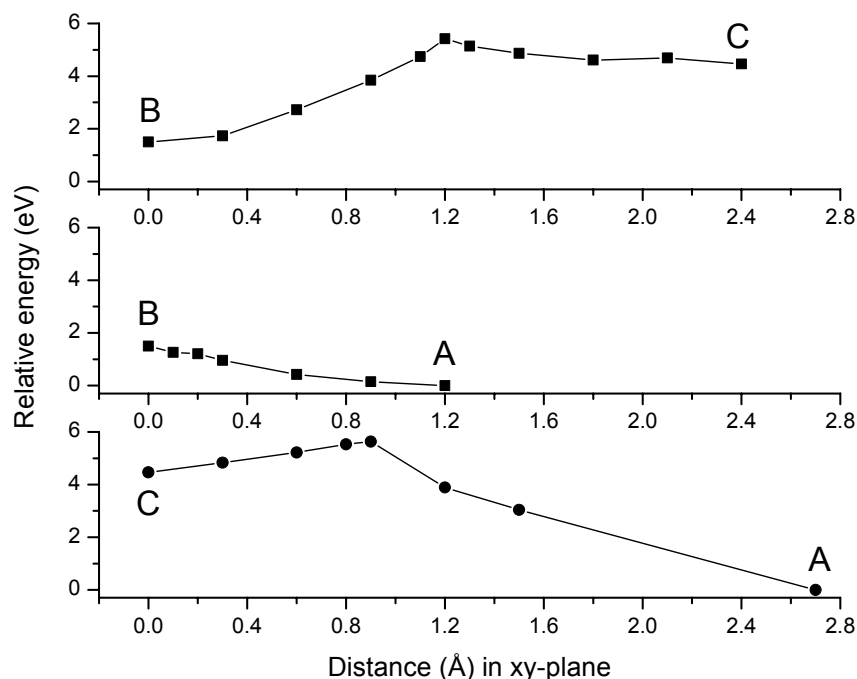


Figure 7.5 Approximate potential energy pathways for migration between the investigated adsorption sites; $A \leftrightarrow B$, $A \leftrightarrow C$, and $B \leftrightarrow C$.

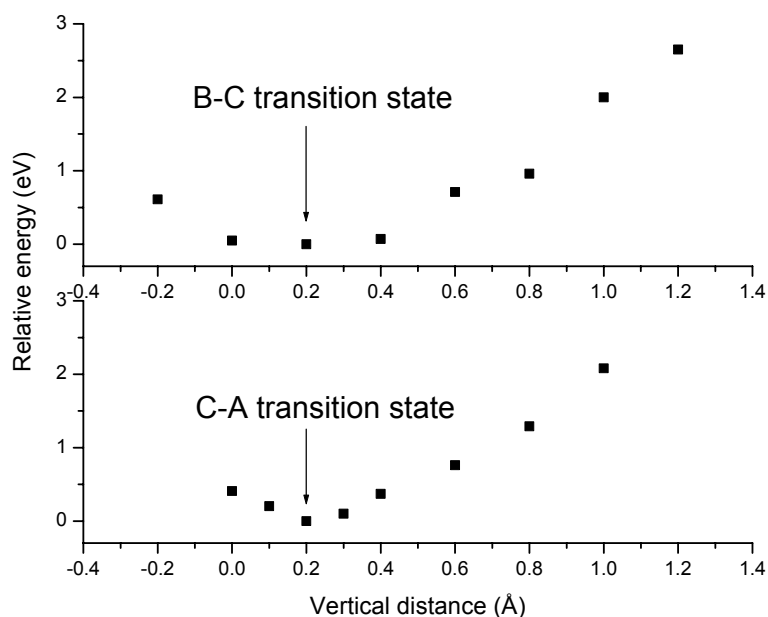


Figure 7.6 Location of real transition state at a vertical distance from the projected one.

Total energies for adsorption at site A, B, C, as well as the total energy for the two transition sites, T_{A-C} and T_{B-C} , were calculated in the GGS approximation. From these energies migration barriers could be calculated, as presented in Table 7.6.

Site	Relative energy (GGS) (eV)		Migr. path	Migr. barr. (eV)
A	0		A→C	9.1
B	1.7		C→A	3.6
C	5.5		B→C	5.4
T_{A-C}	9.1		C→B	1.6
T_{B-C}	7.1		A→B	1.7
			B→A	0

Table 7.6 Migration barriers for specifically chosen pathways on the surface, calculated from the relative total energies.

In order to study the impeding effect of migration barriers on the evolving surface structure, the barriers in correspondence to the individual adsorption energies need to be evaluated (see Table 7.6). Site A, which correspond to the equilibrium

(bulk) position, shows as expected the lowest total energy after adsorption. Energy barriers of 1.7 and 9.1 eV need to be overcome to migrate from this site (A) to B and C, respectively. The former type of migration ($A \rightarrow B$) would most likely result in an immediately reversed migration back to site A, since the barrier for the situation $B \rightarrow A$ is close to zero. It is therefore indicated that if adsorption at the equilibrium site is obtained (i.e. to site A), it is unlikely that the surface evolves further (with migration to a non-crystalline site). The opposite case, initial adsorption at non-equilibrium sites, needs some further considerations: Since a maximum could not be observed for $B \rightarrow A$ migration in Figure 7.5, site B must be situated very close to a transition state (if it exists at all) and, hence, the migration barrier to A is close to zero. Comparing the barriers for migration to A or C (0 and 5.4 eV, respectively) clearly show preferential migration towards site A, and, hence, towards crystallinity. Adsorption at site C, on the other hand, will lead to migration barriers of 3.6 and 1.6 eV, in the A and B direction, respectively. This means that surface migration from C to A will be energetically more favorable if passing site B, i.e. $C \rightarrow B \rightarrow A$, and the minimum barrier for migration is then 1.6 eV.

In order to estimate the effect of this barrier on the evolving surface structure, (and consequently on the film microstructure evolution), one can refer to similar investigations for other materials. Crystalline TiN and ZrO_2 have minimum barriers of 0.35 [37] and 0.4 eV,[38] respectively. Furthermore, amorphous SiO_2 (glass) has corresponding migration activation energies of 4-5 eV.[39] Hence, a comparison to the here presented investigation, show that the most critical barrier (1.6 eV) has a magnitude corresponding to no obvious preference for neither crystalline nor amorphous growth. Instead, the results indicate that the barriers impede surface migration towards an equilibrium structure, at least for kinetically limited film growth.

7.2.4 Effect of ion energy on film microstructure

As previously mentioned, low temperature vapor phase condensation ($\leq 250^\circ C$) of alumina is known to result in an amorphous structure,[29] and understanding the influence of growth parameters (e.g. ion energy) on the atomistic mechanisms that are active during the growth process, is essential for controlling microstructure evolution.

Classical Molecular dynamics (MD) simulations based on empirical potentials have proven to be useful for studying ion-surface interactions. Several material systems have been investigated for this purpose, see for example Ref. 40-45. The questions addressed have been directed towards the influence of impinging ion energy on adatom diffusion / bulk damage,[40] final adatom position,[41] film morphology,[42] film structure / density,[43] surface exchange diffusion,[44] and stress generation.[45] Generally, it was shown that the ion energy is important for these properties/processes.

Ab initio MD may be an alternative to classical MD, where instead of empirical potentials the electronic structure is explicitly treated. Here, the results of first principles simulations within Density Functional Theory (DFT) are presented, simulating collisions between an Al^+ ion and an $\alpha\text{-Al}_2\text{O}_3$ surface. The effect of ion movement on the ion-surface energy transfer mechanism and the geometrical structure is investigated.

The interaction between an Al^+ ion (denoted Al_c) moving towards site C (Figure 7.1) on the O-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface was investigated for initial kinetic energies of 0 and 3.5 eV. The temperature of the system was set to 330 K, and the simulations were performed in time steps of 1 fs. The total simulation time (0.3 ps) chosen corresponds to when the individual atoms oscillate around a momentarily stable average distance from their equilibrium bulk positions, as exemplified in Figure 7.7 (for an ion-surface collision at 3.5 eV).

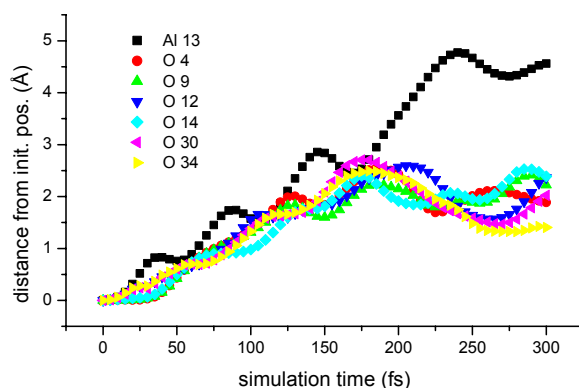


Figure 7.7 Distance from initial equilibrium bulk position vs simulation time for the atoms closest to the collision site (3.5 eV collision energy).

The effect of ion energy on the local temporal structure evolution is presented in Figure 7.8 and 7.9, showing atom/ion coordinates in time steps of 5 fs in the collision between Al_c and the surface. Only nearest neighbors to the collision site are shown. Figure 7.8 presents the result of no initial velocity of Al_c .

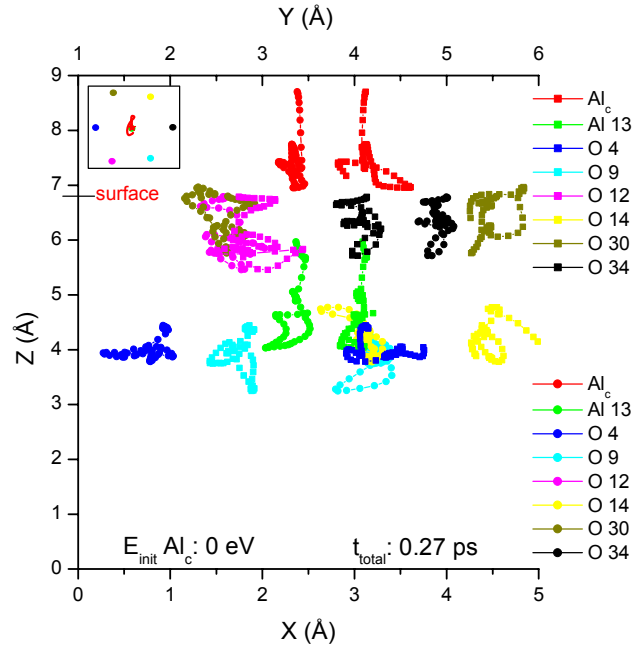


Figure 7.8 Coordinates for an adsorbing Al^+ ion (denoted Al_c) and its closest neighbors in an ion-surface collision event. Initial kinetic energy of Al_c ; 0 eV. (■ = XZ-plane, ● = YZ-plane)

The inserted square is a top view of the surface segment investigated, where the cross and the circles indicate the initial position of Al_c and the neighbors, respectively, and the red line corresponds to Al_c movement in the XY-plane during a simulation time of 0.27 ps. The main graph shows the change in position for the atoms (XZ-plane=■ and YZ-plane=●) during the simulation. To begin with, Al_c is accelerated towards the surface without deviating significantly in x- or y direction, indicating a local potential energy minimum at the underlying surface site. When reaching the surface, Al_c does not penetrate the topmost layer, but diffuses within approximately a 1 Å radius in the XY-direction (see red line in the inserted square). In addition to temperature oscillations (calculated to < 1 fm in amplitude [46]), the surrounding ions move subsequent to adsorption; on average approximately 1 Å from the initial position.

As the initial kinetic energy is increased to 3.5 eV (5 km/s), Al_c penetrates the surface (see Figure 7.9). Larger displacements are observed (as compared to 0 eV energy, in Figure 7.8), for all ions, in both XZ- and YZ-plane, most pronounced in z direction. The largest changes in nearest neighbors distance are between the atom at the collision site (in the second layer) and the topmost surface atoms, with increments above 100 %. (For the 0 eV case, the corresponding values are up to 20 %.) The maximum observed displacement is approximately 4.5 Å, as can be seen in Figure 7.7, while the penetration depth of Al_c is approximately 2 Å. This value is consistent with results from a SRIM-simulation (the Stopping and Range of Ions in Matter [47]) of a similar collision event, which show a corresponding average depth of 2.3 Å.

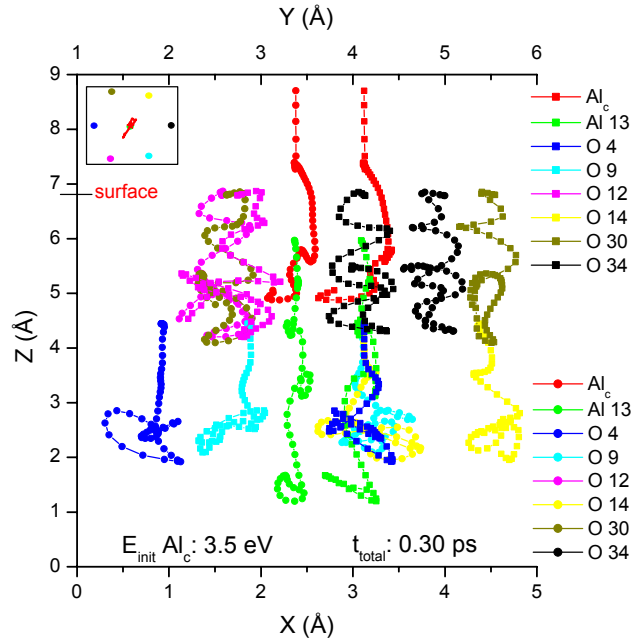


Figure 7.9 Coordinates for an incoming Al^+ ion (denoted Al_c) and its closest neighbors in an ion-surface collision event. Initial kinetic energy of Al_c ; 3.5 eV. (■ = XZ-plane, ● = YZ-plane)

The change in atomic positions is a result of energy transfer associated with the ion-surface interaction, which in turn can be depicted through velocity changes of Al_c , as shown in Figure 7.10a. Independent of the initial velocity (0 or 5 km/s), a velocity increase was detected < 2 Å from the surface, which can be understood by an attractive potential interaction prior to collision. The 0 eV ion is accelerated to ~ 5 km/s, which is comparable to the velocity of the 3.5 eV ion. However, the effect of

the resulting collisions is very different. This apparent contradiction can be understood by considering the velocity as the ions reach the surface: The faster ion collides with the surface after ~ 20 fs simulation time, with a velocity close to the initial value, while the slower ion collides after ~ 50 fs, when its velocity has changed once again and decreased, also approaching its initial value. During the collision event, there is a rapid decrease in velocity, which indicates energy transfer between Al_c and the topmost surface layers. The transferred energy causes distortion of the structural atomic arrangement, to what extent can be seen in Figure 7.10b. The maximum deviation from the initial coordinates is strongly dependent on collision energy, especially for closely underlying atoms, which deviates up to ~ 4.5 Å.

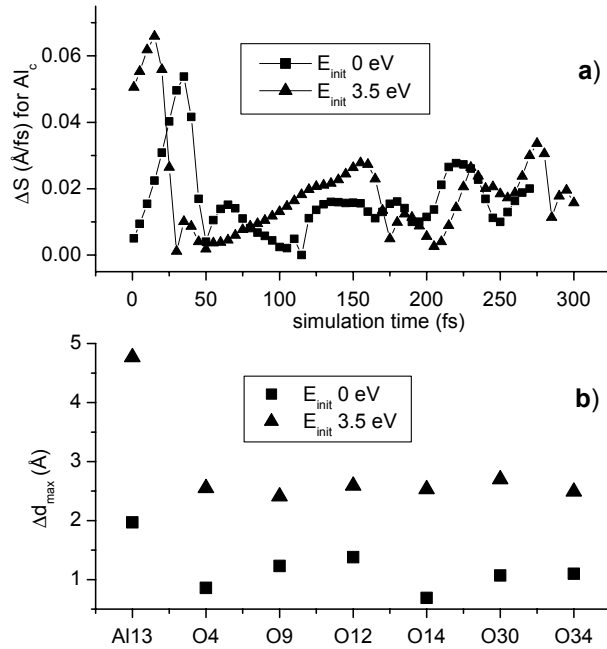


Figure 7.10 a) Change in position (ΔS) per fs (=velocity) for an incoming Al_c vs simulation time.
b) Obtained maximum distance Δd_{max} (Å) from initial position.

A solid is under stress when its atoms are displaced from their equilibrium position. The displacement is governed by interatomic potentials between the atoms, and the magnitude of the displacement results in varying degree of structural changes. Theoretically, a solid obeying a Lennard Jones potential can be strained approximately 11 % before bond breaking occurs.[48] For $\alpha\text{-Al}_2\text{O}_3$, a Buckingham type of potential has been used to describe the interatomic interaction,[49] with an

equilibrium Al-O bond distance of 2 Å. In comparison, the radial distribution function of liquid alumina shows a corresponding bond distance of 1.76 Å,[50] in accordance with MD studies.[51] Using the adsorption-induced changes in atomic positions as a reference, see Figure 7.10b (0 eV), the displacements calculated for the 3.5 eV ion-surface collision are large compared to the bond length: Al 13 has penetrated its underlying atomic layer (initial layer distance 1.52 Å), and moved close to 5 Å from its equilibrium position. In comparison to the 2 Å equilibrium Al-O bond distance, this is a clear indication of bond breaking and subsequent formation of local disorder.

In conclusion, ion-surface collisions have been investigated by means of *ab initio* MD. The time dependent position of the bombarding ion as well as its surrounding neighbors, were studied for initial kinetic energies of 0 and 3.5 eV (0 and 5 km/s, respectively), in order to obtain detailed information about ion-surface interaction prior to the collision event with following local structure evolution. Energy transfer, as indicated by changes in ion velocity, resulted in local structural disorder at a collision energy as low as 3.5 eV.

7.3 Removal of H incorporated in the film

Thin films can be produced by a wide spectrum of vacuum based vapor deposition techniques, which all are characterized by the presence of residual gas. In high vacuum growth systems H₂O is the most abundant residual gas,[52] and a source of hydrogen. Previous studies have shown hydrogen incorporation in alumina thin films.[17] Furthermore, it is well known that bulk alumina forms hydroxides.[53] The unintentional incorporation of hydrogen affects composition and microstructure,[18,22] and hence the material properties.[18] It is therefore desirable to enable growth excluding this incorporation. The amount of hydrogen in strontium titanate films was shown to be strongly affected by substrate temperature.[22] In addition to substrate heating, energy can also be supplied to the growing film through ion bombardment. This was exemplified in a Monte Carlo study [54] on oxygen desorption induced by incident ions on a Ti surface. Here, an ion-surface collision event between an Al¹⁺ ion and an aluminum hydroxide (gibbsite) surface is simulated, investigating the energy dependence of surface reactions including hydrogen.

The hydrogen terminated (001) surface was chosen for the study, which is the experimentally observed preferential cleavage surface.[21] An Al^{1+} ion was initially positioned 2.2 Å above a horizontal O-H bond, see topview of the topmost surface segment with marked collision site in Figure 7.11a. (The particles marked with red are the bombarding Al^{1+} and two hydrogen atoms further discussed below.) A sideview of the initial geometry of the topmost surface layers is shown in Figure 7.11b. The Al^{1+} ion was assigned an initial kinetic energy (in the vertical direction) of 0 and 3.5 eV, and in subsequent simulations the temporal evolution of the ion/atom positions were studied in time steps of 1 fs.

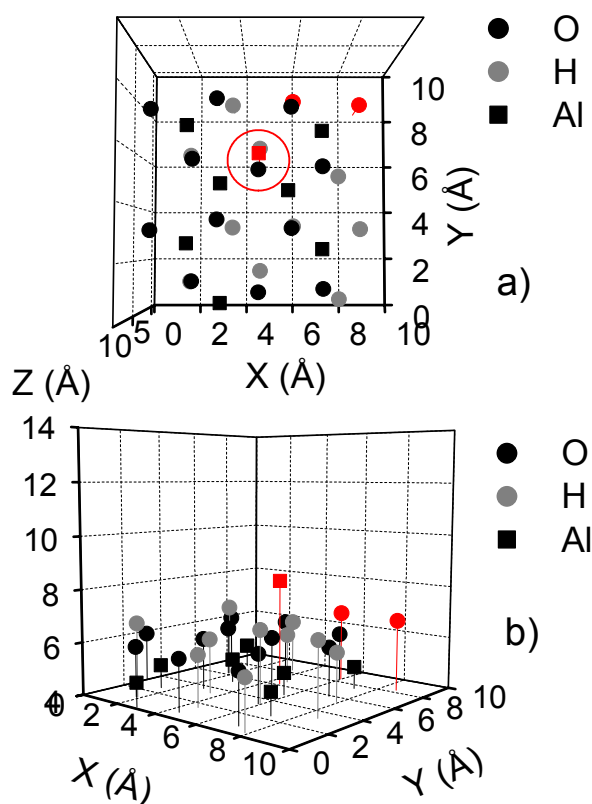


Figure 7.11 a) Topview of the *topmost* surface segment with marked collision site. (In red: the bombarding Al ion and two of the surface hydrogen atoms.) b) Sideview of the same surface segment.

With an initial energy of 0 eV, the Al^{1+} ion was attracted towards the surface, and incorporated in the surface layer, see Figure 7.12a corresponding to the configuration after 0.375 ps. In contrast, the 3.5 eV ion-surface bombardment changed the surface composition, see Figure 7.12b. The Al^{1+} ion approached the surface, stayed

in the top surface layers, and caused (after ~ 0.3 ps) H_2 desorption from the surface. Both simulations were continued for 0.5 ps, but no further changes in surface composition were observed. When comparing the final surface configurations, more outward relaxation is observed for the unchanged surface composition, consistent with previously reported findings of H dependent relaxation of hydrogen terminated $\alpha\text{-Al}_2\text{O}_3$ surfaces.[56]

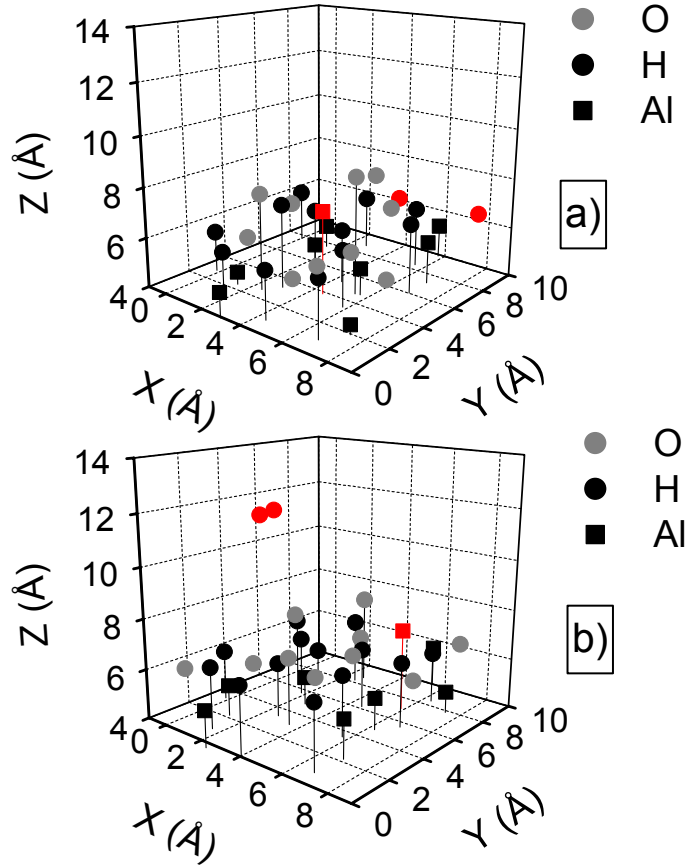


Figure 7.12 a) The configuration after 0.375 ps, for 0 eV initial energy of the bombarding ion.
b) The configuration after 0.375 ps, for 3.5 eV initial energy of the bombarding ion.

When the Al^{1+} ion is assigned 0 eV initial kinetic energy, it moves towards the surface due to attraction. Investigating the subsequent ion-surface collision in more detail, an adsorption induced surface relaxation is observed. A single-point-energy calculation in the gradient corrected approximation (GGA) for the initial and final (after 0.5 ps) configuration of the system shows a decrease in energy by 8.4 eV.

However, the internal energy of the system is here conserved, meaning that there is a corresponding increase in kinetic energy. Energy supplied to a surface through an ion surface collision may enable bond breaking and surface migration. The kinetic energy in this case is evidently not enough to initiate surface migration to an extent to enable hydrogen molecule formation.

As the kinetic energy of the bombarding ion is increased to an initial energy of 3.5 eV, more surface migration is observed. This is exemplified in Figure 7.13a, comparing the interatomic distance during the simulations between the two surface hydrogen atoms marked in Figure 7.11 and 7.12: The interatomic distance decreases around 0.25 ps, leading to bonding and molecule formation. The subsequent molecule desorption from the surface is illustrated in Figure 7.13b, comparing the hydrogen atom-surface distance during the simulations.

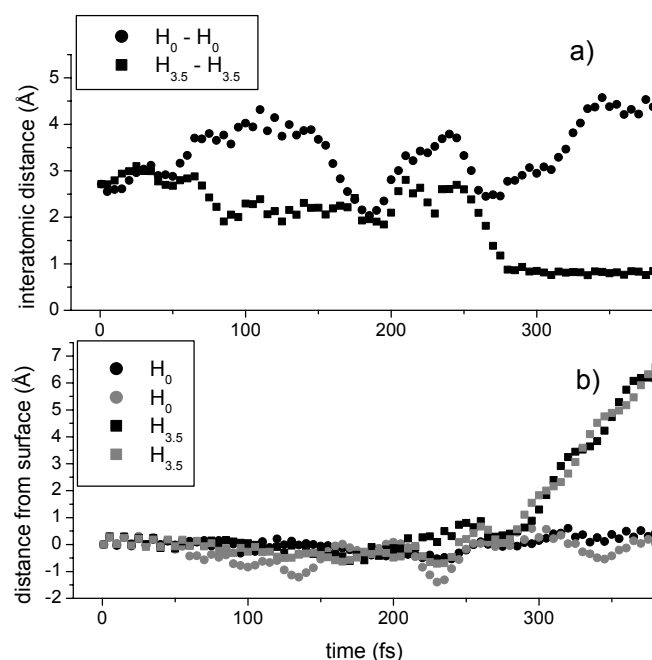


Figure 7.13 The interatomic distance during the simulation, between the two surface hydrogen atoms marked with red in Figure 7.11 and 7.12.

Also here, surface relaxation upon the Al adsorption (and hydrogen desorption) was observed. The calculated (single point energy calculation, GGA) potential energy difference between the initial and final configuration is 10.4 eV, which is 2 eV higher than the previous configuration where there is no change in surface composition upon collision. This may indicate a reaction towards a potential energy minimum of the

system upon molecule formation and removal from the surface, and is consistent with entropy increase as the system approaches equilibrium. However, a study of the oscillation in energy for the last 0.1 ps of the simulation, shows a standard deviation from the average kinetic energy of 1.11 and 0.94 eV for the case of 3.5 and 0 eV initial Al^+ energy, respectively. A corresponding fluctuation can therefore be expected also for the potential energy.

The results presented above can be understood based on thermodynamics. The appropriate thermodynamic potential for the microcanonical ensemble is the entropy [57], and hence corresponds to the function that has its extreme value at thermodynamic equilibrium. Consequently, as the simulation system evolves towards equilibrium, an entropy increase is expected. The results of the simulation can be explained by an activation energy for bond breaking and surface migration being supplied in the 3.5 eV initial kinetic energy simulation, in contrast to the kinetic limitation observed in the low energy simulation. The migration enables H_2 formation. It is straight forward to appreciate that a solid to gas transformation corresponds to an increase in entropy.

The here presented notion that unintentional incorporation of residual gas in thin films can be affected by ion bombardment, is highly relevant for all deposition techniques including low energy ions, such as plasma assisted CVD [58] and PVD. Furthermore, in a study of the effect of gas pressure on the ion energy in cathodic arc plasma, Al^{1+} was found to be the most abundant ion at elevated oxygen pressure. This is exemplified in Figure 7.14, with the fraction of the ions having an energy of > 3.5 eV is about 90 %. Film depositions of Al_2O_3 in the same system (see Chapter 5) showed very low hydrogen incorporation (less than 0.25 at%), which support the here presented notion of affecting hydrogen incorporation by ion bombardment.

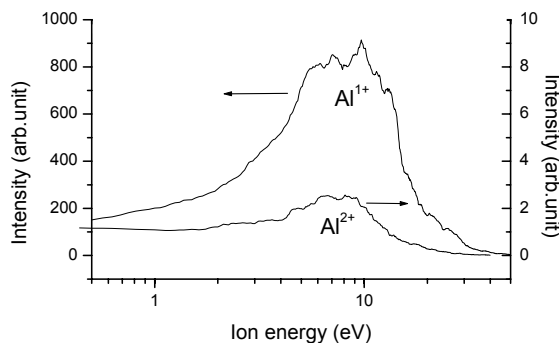


Figure 7.14 Ion energy distributions for Al^{1+} and Al^{2+} in an Al arc plasma at $8 \cdot 10^{-3}$ Torr O_2 .

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8. Summary

This chapter provides a short summary of the experimental and theoretical results presented in this thesis, in addition to suggestions for future research.

8.1 Challenges associated with low temperature growth of alumina

8.1.1 Depositions by cathodic arc

Cathodic arc is the method chosen for the thin film growth related studies presented here, motivated by the high degree of ionization, which is advantageous since the ion energy can be affected by electric fields. The main goal of this thesis is to contribute towards understanding of the correlation between plasma chemistry / ion energy and film composition / microstructure. The plasma, constituting the feed-stock material for the thin film, has therefore been characterized with respect to both chemistry and ion energy.

In this thesis,

- magnetic field dependent plasma chemistry fluctuations

and the

- temporal dependence of the plasma composition within a pulse

have been quantified for reactive, pulsed cathodic arc depositions. It was found that increasing magnetic field strength causes an increase in the pulse-to-pulse fluctuation of the plasma chemistry. Furthermore, evidence was presented for a strong temporal

dependence of the plasma composition *within* the pulse. A large non-metal fraction was observed in the plasma in the beginning of the pulse, and as the pressure increased, this fraction increased both in amplitude as well as in time after arc ignition. Also the metal ion composition was a strong function of both time and pressure, with higher charge states in the beginning of the pulse and at lower pressures. This temporal dependence of the plasma composition can be understood by effects of compound layer formation at the cathode surface and plasma-gas interaction.

Further plasma analysis of a DC cathodic arc plasma showed

- charge dependent ion energy distributions with ions in excess of 200 eV.

In vacuum, higher energies were measured for higher charged ions, as explained by acceleration due to pressure gradient and electron-ion coupling. Introduction of a magnetic field resulted in broader distributions and increased average ion energies, showing that the IEDs can be modified by suitable magnetic field configuration. Introducing oxygen resulted in decreasing energies. With increasing oxygen pressure the average ion energies decreased, though with the tail of the IED extending above 100 eV.

The above presented results show that the plasma composition is time dependent and that the ion energy distributions are charge state dependent. Understanding of these correlations may enable tailoring of materials properties.

8.1.2 Structure / Composition

A: Theoretical investigations

Several theoretical studies were performed to obtain atomic level information of surface processes relevant for structure evolution during alumina film growth. *Ab initio* calculations as well as *ab initio* molecular dynamics simulations based on DFT was used for this purpose. From 0 K calculations, evidence for

- adsorption energies dependent on surface site, species, and charge state of ion and
- presence of migration barriers on the surface

was presented. The adsorption process of ions identified in the plasma chemistry characterization was studied at different surface sites. All adsorption reactions were found to be exothermic, and adsorption on the equilibrium (bulk) lattice position

resulted in the most preferred adsorption situation. A comparison between adsorption energies indicated that amorphous film growth may be likely to occur with Al^{3+} and O^+ ions as film-forming material. The presence of migration barriers was also studied, where barriers of 1.6 eV indicate that activation energy may be necessary to form the equilibrium surface structure. These results may explain the experimentally observed formation of amorphous structures during kinetically limited alumina thin film growth.

Additional information concerning structural evolution could be gained from a MD simulation of ion-surface collision, showing

- local structural disorder at collision energies as low as 3.5 eV.

Due to presence of residual gas, the compositional evolution during deposition may result in the formation of an hydroxide instead of an oxide. Therefore, the effect of ion energy on hydroxide surface reactions was investigated for an ion-surface collision. The simulation results suggest that

- hydrogen desorption upon ion-surface interaction may be possible.

For 0 eV initial kinetic energy of the incident ion, no change in surface composition was observed. An increase in energy to 3.5 eV showed extended surface migration of hydrogen, with subsequent H_2 formation and desorption. These results may be understood by thermodynamic principles, and an increase in entropy upon H_2 formation.

B: Experimental investigations

Experiments were performed to investigate the effect of ion energy and substrate temperature on the film composition and microstructure. Major conclusions were

- structure evolution strongly dependent on ion energy
- and
- γ -alumina formation as low as 200 °C.

Decreasing the substrate bias potential from –50 to –100 V caused the amorphous or weakly crystalline films to evolve into stoichiometric, crystalline films with a mixture of the α - and γ -phase above 700 °C, and clearly γ -phase dominated films at temperatures as low as 200 °C. All films had a grain size of < 10 nm, suggested to be correlated to the high ion energies observed in the plasma characterization. The

combined constitution and grain size data is consistent with previous work stating that γ -alumina is thermodynamically stable at grain sizes < 12 nm.

Additional analysis of the film composition showed

- low concentration of impurities.

ERDA analysis of the films showed a hydrogen content of less than 0.25 at%. The result may be explained by hydrogen removal upon ion bombardment, as suggested in the theoretical study presented above.

The results presented in this section provide new insights into the correlation between plasma chemistry / ion energy and film composition / film microstructure, and may at least in part explain the experimentally observed formation of amorphous alumina during kinetically limited growth. These results may also provide pathways to a) crystalline film growth at low temperatures, as well as to b) a reduction of the impurity incorporation during deposition.

8.2 Future work

During this thesis several exciting questions have surfaced. Hence, suggestions for possible future work are presented below.

8.2.1 Plasma related studies

Since the plasma is the film forming material, controlling the plasma composition is a highly important tool for tailoring film properties. As previously mentioned, cathodic arc is advantageous due to the high degree of ionization. However, the high charge states commonly observed results in broad total ion energy distributions, especially when using a substrate bias potential. Therefore, a reduction of the charge states would be the first issue to address, preferably changing the metal ion content to only include Al^{1+} . A decrease of the charge states has been observed when increasing the pressure in the chamber, and hence a further increase, possibly including both oxygen and argon, would be of interest. Moreover, this would result in narrower charge-state-resolved ion energy distributions, which is beneficial for controlling the ion energy. Also the magnetic field strength affects the charge states,

and a reduction of the field strength in the plasma filter would decrease the concentration of highly charged ions. When the desired plasma composition has been achieved, preferably Al^{1+} ions with energies in a well defined narrow range, the correlation between plasma properties / ion energies and the thin film can be further investigated.

8.2.2 Thin film growth

With the well defined plasma described above, a similar film growth study as described in this thesis can be performed. The separate effects of ion energy and substrate temperature on the film composition and constitution would be investigated in more detail. A likely consequence of the actions taken to obtain lower charge state, is a lower deposition rate. However, longer depositions may be beneficial in terms of an increased diffusion. The grain size is well known to affect material properties, and therefore a detailed analysis of the correlation between deposition conditions and grain size would be of interest.

8.2.3 Theoretical studies

Some light has been shed on the adsorption process of different ions on an alumina surface. Extending this study to also include ions stemming from residual gas, and molecules of O_2 , H_2O and H_2 may further illuminate structural as well as compositional evolution during film growth. An expanded study of the hydrogen desorption upon ion-surface interaction would also be of interest: To distinguish between effects of temperature and energy supplied from bombarding ions, an initial investigation would concern hydroxide surface reactions *without* ion irradiation, varying both hydrogen coverage and temperature. Additional information could be gained when comparing to results of the adsorption study, which also provide quantification of the potential energy of the system. A continued study would include supply of energy from bombarding atom/ion. Ion-surface collisions are accompanied by charge transfer, which may affect subsequent surface reactions. Al^{1+} was investigated in this thesis, and corresponding simulations for neutral Al as well as higher charged Al ions would be of interest.

RESUMÉ

NAME: EVA JOHANNA LOVISA ROSÉN

PLACE / DATE OF BIRTH: Habo, 28-04-1975

NATIONALITY: Swedish

EDUCATIONAL RANGE OF EXPERIENCE

In Germany:

RWTH Aachen (Materials Chemistry), Ph.D. student, Jan 2003 – present.

In Sweden:

Linköping University (Thin Film Physics), Ph.D. student, Nov 2000 – Jan 2003.

Linköping University, Project employee, Sept 2000 – Nov 2000.

Linköping University, Master's Programme in Physics, Aug 1995 – Aug 2000

Tranås Gymnasium, Natural Science Programme, Aug 1991 – Aug 1994

QUALIFICATIONS

- Filosofie Licentiate (Fil. Lic.), Dec 2002.

Thesis title: "Characterization of Metal Plasma Streams from Arc Discharges in a Reactive Environment"

Main subject: Thin Film Physics, Branch of studies: Materials Science.

- Master of Science (M. Sc.), Aug 2000.

Diploma work title: "Limiting Charge Concentration in Doped Polymers: A Monte Carlo Study"

Main subject: Physics, Branch of studies: Theoretical Physics