Alternative method for deposition of alumina thin films

Daniel Magnfält
Examensarbetet utfört vid Plasma och beläggningsfysik, IFM
2009-01-30
LITH-IFM-A-EX--09/2046—SE
Alternative method for deposition of alumina thin films

Daniel Magnfält

Examensarbetet utfört vid Plasma och beläggningsfysik, IFM

2009-01-30

Handledare
Erik Wallin

Examinator
Ulf Helmersson
Alternative method for deposition of alumina thin films

Författare
Author
Daniel Magnfält

Sammanfattning
Abstract
Deposition of alumina thin films in the presence of fluorine as a method for reducing the hydrogen incorporation in the films was investigated in this thesis. Hydrogen incorporated in alumina thin films have been shown to cause a lower density and refractive index in amorphous films, assist electrical conduction through thin amorphous films as well as inhibiting the formation of the thermally stable α-phase.

The depositions were made in a ultra high vacuum system where high vacuum conditions were simulated by leaking water vapor into the system. No substrate heating or substrate bias was applied. Films were deposited at a range of fluorine partial pressures, from $2 \times 10^{-5}$ to $5 \times 10^{-5}$ Torr, and were analyzed by elastic recoil detection analysis, nuclear reaction analysis, scanning electron microscopy and x-ray diffraction. Mass spectrometry measurements were done during the depositions to analyze the deposition process.

The mass spectrometry investigations show that there is a trend of increasing O$_2$ partial pressures with increasing fluorine partial pressures during the depositions. This is ascribed to the well known reaction: $2H_2O + 2F_2 \rightarrow O_2 + 4HF$. However, no trend in the measured water partial pressures can be observed. The increase in the O$_2$ partial pressure is therefore attributed to a reaction between water and fluorine on the chamber walls. The chemical analysis show that the hydrogen incorporation in the films were lowered from ~10 at.% when deposited in the presence of water vapor to ~3 at.% when deposited in the presence of water vapor and ~2 $\times 10^{-5}$ Torr fluorine. The hydrogen incorporation stabilize at ~3 at.% at higher fluorine partial pressures. However, there is also a large amount of fluorine incorporated in the films, ~20 at.% with a fluorine partial pressure during the deposition of ~46 at.% with a fluorine partial pressure of ~$5 \times 10^{-5}$ Torr. There is a slight increase in the aluminum concentration in the films deposited with fluorine. This is attributed to bonding the hydrogen in aluminum hydroxide while the reminder forms Al$_2$O$_3$ or AlF leading to an increase in the aluminum concentration in the film. A linear decrease in the deposition rate with increasing fluorine partial pressures during the deposition was observed, this can be explained by sputter etching of AlF$_x$ and AlO$_x$F$_y$ by energetic O$^-$ ions. The XRD investigation show that the films deposited with the highest fluorine partial pressures were x-ray amorphous, the films with deposited with lower fluorine partial pressures are therefore also assumed to be amorphous.

Nykeltalr
Keyword
Alumina, RF-sputtering, hydrogen, fluorine, amorphous alumina
Abstract
Deposition of alumina thin films in the presence of fluorine as a method for reducing the hydrogen incorporation in the films was investigated in this thesis. Hydrogen incorporated in alumina thin films have been shown to cause a lower density and refractive index in amorphous films, assist electrical conduction through thin amorphous films as well as inhibiting the formation of the thermally stable α-phase.

The depositions were made in a ultra high vacuum system where high vacuum conditions were simulated by leaking water vapor into the system. No substrate heating or substrate bias was applied. Films were deposited at a range of fluorine partial pressures, from \(2.5 \cdot 10^{-8} - 5 \cdot 10^{-5}\) Torr, and were analyzed by elastic recoil detection analysis, nuclear reaction analysis, scanning electron microscopy and x-ray diffraction. Mass spectrometry measurements were done during the depositions to analyze the deposition process.

The mass spectrometry investigations show that there is a trend of increasing \(O_2\) partial pressures with increasing fluorine partial pressures during the depositions. This is attributed to the well known reaction: \(2H_2O + 2F_2 \rightarrow O_2 + 4HF\). However, no trend in the measured water partial pressures can be observed. The increase in the \(O_2\) partial pressure is therefore attributed to a reaction between water and fluorine on the chamber walls. The chemical analysis show that the hydrogen incorporation in the films were lowered from \(\sim 10\) at.\% when deposited in the presence of water vapor to \(\sim 3\) at.\% when deposited in the presence of water vapor and \(2 \cdot 10^{-5}\) Torr fluorine. The hydrogen incorporation stabilize at \(\sim 3\) at.\% at higher fluorine partial pressures. However, there is also a large amount of fluorine incorporated in the films, \(\sim 20\) at.\% with a fluorine partial pressure during the deposition of \(2 \cdot 10^{-5}\) Torr and \(\sim 46\) at.\% with a fluorine partial pressure of \(5 \cdot 10^{-5}\) Torr. There is a slight increase in the aluminum concentration in the films deposited with fluorine. This is attributed to bonding the hydrogen in aluminum hydroxide while the reminder forms \(Al_2O_3\) or \(Al\) leading to an increase in the aluminum concentration in the film. A linear decrease in the deposition rate with increasing fluorine partial pressures during the deposition was observed, this can be explained by sputter etching of \(AlF_x\) and \(AlO_xF_y\) by energetic \(O^−\) ions. The XRD investigation show that the films deposited with the highest fluorine partial pressures were x-ray amorphous, the films with deposited with lower fluorine partial pressures are therefore also assumed to be amorphous.
Acknowledgements

I would like to thank:

Ulf Helmersson for giving me the opportunity to do this project and for being willing to answer my questions.

Erik Wallin for being an excellent supervisor and for always taking the time to help me with practical as well as theoretical problems even though he was writing his PhD thesis.

Petter Larsson for helping me with my vacuum and mass spectrometer related troubles.

The rest of the Plasma & Coatings Physics group and the Thinfilm Physics and Nanostructured Materials groups for making this a great place to work and for all the Friday fikas.

My family for their support throughout my studies.
Contents

1 INTRODUCTION .................................................................................................................. 1
2 ALUMINA .......................................................................................................................... 2
3 THIN FILM DEPOSITION ................................................................................................. 3
  3.1 CHEMICAL VAPOR DEPOSITION ................................................................................. 3
  3.2 PHYSICAL VAPOR DEPOSITION .................................................................................. 3
  3.3 SPUTTERING .................................................................................................................. 3
    3.3.1 Magnetron Sputtering ............................................................................................ 4
    3.3.2 Radio Frequency Sputtering .................................................................................. 5
4 CHARACTERIZATION TECHNIQUES ............................................................................... 6
  4.1 MASS SPECTROMETRY ................................................................................................. 6
  4.2 SCANNING ELECTRON MICROSCOPY ........................................................................ 6
  4.3 X-RAY DIFFRACTION ................................................................................................... 7
  4.4 ION BEAM ANALYSIS ................................................................................................. 7
    4.4.1 Elastic Recoil Detection Analysis ............................................................................ 7
    4.4.2 Nuclear Reaction Analysis .................................................................................... 8
5 EXPERIMENTAL DETAILS ............................................................................................. 9
6 RESULTS AND DISCUSSION .......................................................................................... 11
  6.1 FILM DEPOSITION ......................................................................................................... 11
  6.2 MASS SPECTROMETRY ................................................................................................. 11
  6.3 FILM CHARACTERIZATION ......................................................................................... 12
    6.3.1 Scanning Electron Microscopy .............................................................................. 13
    6.3.2 Nuclear Reaction Analysis .................................................................................... 14
    6.3.3 Elastic Recoil Detection Analysis ........................................................................... 16
    6.3.4 X-Ray Diffraction ................................................................................................. 19
7 CONCLUSIONS .................................................................................................................. 21
8 FUTURE WORK ................................................................................................................. 22
9 REFERENCES ..................................................................................................................... 23
1 Introduction

Alumina or aluminum oxide is an insulating and transparent material with a high hardness and chemical stability. These properties have lead to it being used in a wide range of applications such as optics, wear-resistant coatings for cutting tools and insulating layers in semiconductor devices.

Alumina thin films are currently deposited using various physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods. Although CVD have been more commonly used in commercial applications than PVD for depositing alumina thin films, deposition by PVD, such as magnetron sputtering, is gaining popularity because it, unlike CVD, allows for low temperature depositions and deposition of the meta-stable phases of alumina. However, magnetron sputtering and other PVD techniques on an industrial scale are performed in high vacuum environments where residual gases mostly consisting of water vapor are present. It has been shown that water contamination inhibits the formation of the hard and thermally stable $\alpha$-phase of alumina and also leads to hydrogen incorporation in the films which reduces the refractive index and the elastic modulus of amorphous alumina films.[1][2][3]

This thesis investigates a new method to reduce the amount of residual water in a sputter deposition system by the introduction of fluorine with the sputter gas and the resulting effects on hydrogen incorporation in alumina thin films.
2 Alumina

Aluminum oxide or alumina (Al₂O₃) occurs naturally in several forms e.g. in the mineral corundum, ruby and sapphire. These minerals all consist of the crystalline α-phase of alumina. Corundum is pure alumina while ruby is alumina doped with small amounts of chromium and sapphire is alumina doped with iron and titanium.

The α-phase is the only thermodynamically stable phase of alumina and is in its single crystalline form also known as sapphire. There are also several meta-stable phases of alumina e.g. γ-, κ- and θ-alumina, which all transform through a series of meta-stable phases to the α-phase when heated. The α- and κ-phases have been used as wear-resistant coatings deposited by CVD for decades because of their chemical stability, good mechanical properties and in the case of κ-alumina the high transition temperature while γ-alumina is used in catalyst applications due to the low surface energy and high surface areas.[4][5][6] Amorphous alumina and α-alumina are also used in electrical and optical applications because of the insulating properties and transparency of alumina.[7][8] α-alumina have a hardness of ~28 GPa and an elastic modulus of ~440 GPa[9] while amorphous alumina have a hardness of ~11 GPa and an elastic modulus of ~160 GPa[10] which can be compared to diamond that have a hardness of ~100 GPa and an elastic modulus of ~1100 GPa[11].

The influence of residual water in the deposition system on the properties of alumina films have been investigated by several groups. It has been shown that the incorporation of hydrogen in the form of aluminum oxide hydroxide (AlOOH) in alumina films reduces the density of the film and is therefore the reason of the low refractive index measured for alumina films.[1] Incorporation of hydrogen also lowers the elastic modulus of amorphous alumina significantly.[2] The presence of residual water also promotes γ-alumina formation over α-alumina[3] and amorphous alumina[2] during sputter deposition. Interstitial hydrogen has also been found to contribute to conduction through thin amorphous alumina films via a defect level introduced by the hydrogen[12].

No investigations of sputter deposition of alumina films in the presence of fluorine have been made. However, both Fu et al[13] and Lie et al[14] have found that the addition of AlF₃ to the precursor lowers the transition temperature from the θ-phase to the α-phase by 300°C when synthesizing alumina by wet chemical methods.
3 Thin Film Deposition

Thin film deposition methods are generally divided into two main categories, Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD), depending on how the mass transport of the deposited materials is manifested.

Since the work in this thesis was made using Radio Frequency (RF) sputtering, a PVD technique, the emphasis of this chapter will be on sputtering techniques in general and RF sputtering in particular. It should also be noted that the information in this chapter is from Ohring[15] unless anything else is mentioned.

3.1 Chemical Vapor Deposition

CVD processes are used for thin film deposition because of their great versatility. They can be used to deposit a large number of materials with varying stoichiometries and high deposition rates compared to PVD processes. This versatility combined with affordable equipment and operation costs makes CVD processes common in industry applications.

CVD processes utilize volatile gases that react chemically to form a solid. These reactions usually require high substrate temperatures to take place. The high substrate temperatures are a problem since different thermal expansion coefficients for the substrate and the film may lead to cracks in the film when the film is cooled. The high temperatures used also limits the choice of substrate materials. Since the gases in and the by-products from CVD processes often are toxic, flammable, pyrophoric and/or corrosive safety measures have to be taken to ensure that both personal injuries and environmental hazards are avoided.

3.2 Physical Vapor Deposition

In PVD processes the source material is a solid or a liquid where atoms are evaporated or sputtered from the source in vacuum, transported to and condensed on the substrate.

Several evaporation techniques are in use today but they all work on the same principle. The source material is heated under vacuum conditions to a high enough temperature to melt or sublime. The evaporated atomic gas is then transported to the substrate where it is condensed. Several techniques for achieving evaporation are employed. The most common ways of heating the material are resistive heating, electron beam heating or heating by high power pulsed laser. Evaporation techniques have high deposition rates and can be used to deposit films far from thermal equilibrium. There is however difficulties with achieving a uniform film thickness, especially if the substrate is stepped or have trenches as well as maintaining film stoichiometry when evaporating from compound sources.

3.3 Sputtering

Instead of using heat to provide the source atoms with kinetic energy as in evaporation techniques atoms can also be ejected by bombarding the material source, or target, with ions from a plasma. The plasma in sputtering systems is an ionized gas, usually argon, consisting of neutral atoms, positive ions and free electrons.
A sputtering system consists of a vacuum chamber with a cathode, the sputtering target, a grounded anode, usually the vacuum chamber wall, and the substrates which can be given an arbitrary potential. In DC sputtering a negative DC voltage is applied to the cathode while the anode is grounded. The sputter gas pressures are usually between a few millitorr and a hundred millitorr. The sputtering process starts when the plasma is ignited. The gas ions are then accelerated towards the cathode. When they hit the cathode several things happen. Atoms are ejected, or sputtered, from the target through momentum transfer in the collisions. Impacting ions might also cause a collision cascade in the target where one target atom impacts another target atom and so on until all kinetic energy is lost and no atom is ejected, impacting ions might also be recoiled off the target. Negative ions, adsorbed species, photons and secondary electrons are also released from the target.

The secondary electrons are necessary for the sputtering process as they ionize gas atoms maintaining the plasma. However, many of the emitted electrons will travel to the walls of the system and be lost before they ionize any atoms.

### 3.3.1 Magnetron Sputtering

Charges moving in an electromagnetic field are subject to the Lorentz force which states that charges moving on trajectories non-parallel to the field lines of a magnetic field will be subject to a force bending the charge trajectory. The charges will therefore travel along the field lines with a corkscrew motion. This effect is used in magnetron sputtering where a magnetron is placed behind the target as shown in Figure 1. The magnetic field from the magnetron will confine the electrons near the target prolonging their lifetime and increasing the probability of ionizing collisions with gas atoms. This results in a denser plasma confined closer to the target by the magnetic field than in non-magnetron sputtering with the same process parameters. The confinement leads to an eroded region, a so-called racetrack, on the target since the sputtering is most intense where the plasma density is the highest. The higher plasma density can be used to achieve several things such as higher deposition rates, lower operation voltage or a lower sputter gas pressure.
These advantages have made magnetron sputtering the standard sputter deposition technique.

### 3.3.2 Radio Frequency Sputtering

Deposition of insulating materials such as Al₂O₃ from compound targets by DC sputtering is not practically possible because of the impossibly high voltages required to draw a current through the target. Instead a high frequency AC signal, usually 13.56 MHz since it is reserved for plasma processing, is applied to the target. The high frequency allows for power to be coupled through electrodes with any impedance allowing for insulating targets to be used. The high frequency gives the free electrons oscillating between the plasma sheaths an energy that is high enough for ionizing gas atoms, therefore there is no need for secondary electron emission to sustain the plasma. The ions in the plasma, which are heavy compared to the electrons, cannot follow the oscillations of the electric field. As a result of this only very few ions, compared to DC sputtering, would reach the target. Sputtering is instead achieved because the target self-biases to a negative potential. This occurs since electrons are much more mobile than ions. The target will therefore attract more electrons on the positive half cycle than it will attract ions on the negative half cycle resulting in an effective negative target bias. The negatively biased target will then attract ions resulting in sputtering. RF-sputtering of compound targets is usually a process with a low deposition rate because of the high bond energy between the atoms in the target results in a low sputtering yield.
4 Characterization Techniques

Several characterization techniques were used during the work on this thesis. They are briefly described in this chapter.

4.1 Mass Spectrometry

Mass spectrometry is an analysis technique commonly used to characterize the composition of gases in an environment by measuring the mass-to-charge ratio of the species. For this to be possible the species must be ionized which, in mass spectrometers, often is achieved by having energetic electrons emitted from e.g. a tungsten filament interacting with the species in a process known as impact ionization. The result is an expelled electron and ionization of the species if the energy transfer in the interaction is high enough.

The ions are then filtered according to their mass-to-charge-ratio and detected. This can be achieved by several techniques with the most common being time-of-flight measurements and quadrupole mass filters. In the present work a quadrupole mass spectrometer has been used. A quadrupole is made up of four parallel circular or hyperbolic rods to which alternating voltages are applied. The ions enter the quadrupole travelling parallel to the rods and are made to oscillate between the rods by the alternating voltages. The amplitude of the ions oscillations depend on the mass-to-charge-ratio of the ions and the magnitude of the voltages of the quadrupole rods. Only ions in a certain mass-to-charge-ratio range will be transmitted through the quadrupole. Ions with lower mass-to-charge-ratios will get unstable trajectories, collide with rods and discharge while ions with higher mass-to-charge-ratios will be lost because they are poorly focused. The transmitted ions are then detected by a faraday cup or electron multiplier detector. Mass spectrometry data requires some interpretation since doubly ionized species as well as different isotopes are detected separately, it is also common that large complicated molecules are split into smaller parts during the ionization.[16]

4.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a commonly used tool for material characterization. It produces high resolution images of the sample surface with a large depth of field. No particular sample preparation is needed for imaging conducting samples although insulating samples may need to be coated with a thin conducting film in order to avoid charge build-up on the sample surface.

In an SEM a finely focused electron beam is scanned over the sample surface. The beam electrons interact with material in the near surface region resulting in the emission of secondary electrons with a low energy, x-rays, high energy back scattered electrons and Auger electrons. The secondary electrons are detected and the signal amplified for each image point building up the image. The emitted x-rays are characteristic for the elements in the sample and can be used to measure the composition of the sample in the spot irradiated by the electron beam. This technique is called energy dispersive x-ray analysis or EDX.[15]
4.3 X-ray Diffraction

X-rays incident on a crystal are diffracted in the atomic planes of the crystal. Bragg’s law, \( 2d \sin \theta = n\lambda \), will apply if the wavelength of the x-rays, \( \lambda \), satisfies the condition \( \lambda \leq 2d \), where \( d \) is the plane spacing in the crystal, \( \theta \) is the incidence angle of the x-rays measured from the plane and \( n \) is an integer. It says that constructive interference between x-rays reflected in different planes will occur if the path difference for the x-rays is equal to an integer number of wavelengths. In practice this means that the intensity of x-rays reflected in a sample will vary with the incidence angle giving a high reflected intensity where constructive interference occurs.[11] This can be used to identify the crystal structure of samples since constructive interference only occur in specific lattice planes.

![Schematic picture showing diffraction according to Bragg's law.](image)

**Figure 2:** Schematic picture showing diffraction according to Bragg's law.

One of the most common techniques of for making diffractograms is by simultaneously scanning the incidence angle, \( \theta \), and the diffraction angle, \( 2\theta \). This scanning mode is called \( \theta/2\theta \). Because substrate peaks tend to dominate diffractograms of thin films obtained by \( \theta/2\theta \) scans another scanning technique is usually used for thin films, grazing incidence x-ray diffraction. In grazing incidence x-ray diffraction the incidence angle is fixed at a low angle and only the detector is scanned. This gives a lower penetration depth of the beam and therefore a higher relative intensity of the film peaks.

4.4 Ion Beam Analysis

There are several different ion beam techniques for thin film composition analysis and depth profiling. The most common is Rutherford back-scattering (RBS). However, due to the low sensitivity to light species, e.g. hydrogen, of RBS elastic recoil detection analysis (ERDA) and nuclear reaction analysis (NRA) were used for this work instead.

4.4.1 Elastic Recoil Detection Analysis

In ERDA the sample is bombarded by an ion beam with a low angle of incidence and an energy of several MeV. The ions collide elastically with atoms in the sample which recoil out while other ions forward scatter out of the sample. By measuring the energy of the recoiled and forward scattered ions it is possible to identify the atomic species of the sample. The energy of the recoiled atoms depend on the energy and mass of the incoming...
ions, which is known, as well as the mass of the recoiled atoms and the stopping power of the sample. The collision cross-sections between the incident ions and the atoms involved give the probability of the scattering events and are together with the number of recoiled atoms used to determine the concentrations of atoms in the sample. The energy spectrum from ERDA measurements is complicated since it contains both the forward scattered ions and the recoiled atoms and must be analyzed using software taking these factors as well as the experimental setup into account to give the sample composition as well as depth profiles.[17]

4.4.2 Nuclear Reaction Analysis

Nuclear reaction analysis, or nuclear radiation analysis, (NRA) is another ion beam technique for composition analysis of thin films. It takes advantage of the fact that some incident ions cause a nuclear reaction with the atoms in the sample. During the reaction an excited intermediate nucleus decays into its ground state by emission of $\alpha$-, $\beta$- and/or $\gamma$-particles. This can be used to identify certain elements in a sample since the energies of the emitted particles is unique for every reaction.

NRA is often used for depth profiling of hydrogen where the reaction $^{15}N + {}^1H \rightarrow ^{12}C + ^4He + \gamma$ is utilized by detecting the $\gamma$-ray yield. This reaction has a narrow resonance around 6.385 MeV which can be taken advantage of to do hydrogen depth profiling. This is because the energy of the incident particles determines the depth of the reaction, a higher ion energy therefore gives a larger reaction depth. The depth of the reaction can then easily be determined using the stopping power of the sample and energy of the incident ions. The hydrogen concentrations are determined both by using a standard and without a standard. NRA can also be used to test the bond stability of hydrogen by continually measuring the hydrogen concentration on the same spot over a long time.[17]
5 Experimental Details

The depositions were made in an ultra high vacuum (UHV) system, with a base pressure of $<5 \times 10^{-8}$ Torr for the reference films and $<1 \times 10^{-6}$ Torr for the films sputtered in an H$_2$O containing atmosphere, to ensure low amounts of contaminants and to increase control over the deposition conditions. The vacuum system was modified by the addition of one leak valve for water vapor and an additional gas inlet and connection to the Ar/F$_2$ gas bottle. Both connections were extensively leak tested to ensure that no leaks were present.

Vapor of deionized water was leaked into the system at a pressure of $1 \cdot 10^{-5}$ Torr to mimic the residual gas of a high vacuum system. The leak valve was heated by a resistive heater to a temperature of between 130 and 140 °C during all depositions to prevent ice formation in the valve which otherwise might lead to fluctuations of the water vapor partial pressures in the chamber.

Two sputtering gas mixes were used, Ar of 99.9997 % purity and an Ar/F$_2$ mixture containing Ar of 99.9997 % purity mixed with 1% F$_2$, with a total gas pressure of 5 mTorr for all depositions. The pure Ar flow was controlled by a mass flow controller while the Ar/F$_2$ mixture flow was controlled by a leak valve. The gas concentrations in the chamber during depositions were measured by a differentially pumped mass spectrometer (Spectra Vision 1000-P). Because the mass spectrometer was mounted to a valve that was closed between each deposition the mass spectrometry data was normalized with respect to the main Ar peak to cancel out differences in peak intensities resulting from different valve openings.

A 50 mm Al$_2$O$_3$ (99.99% purity) compound target with a thickness of 3 mm was placed in the on-axis position in the chamber. The target magnetron was powered by an RF power supply (Advanced Energy RFX-600) operating at 13.56 MHz, the RF power used during the depositions was 80 W.

The films were deposited on 18x18 mm Si(100) substrates with no substrate heating applied and a floating bias. The substrates were cleaned in an ultrasonic bath for 5 minutes in acetone followed by 5 minutes in isopropanol and were subsequently blow dried with dry N$_2$. The samples were then inserted into the load-lock chamber of the vacuum system. After the depositions the substrates were left in the vacuum system overnight with the H$_2$O leak valve and the gas inlets closed to allow the chamber to be pumped down as not to contaminate the transfer tube and load-lock with water.

The deposition time for the reference films deposited in a clean chamber as well as for the films deposited with the Ar/F$_2$ gas mixture was four hours while the deposition time for the reference films deposited in $1 \cdot 10^{-5}$ Torr H$_2$O was 5 hours. Three substrates were deposited during each deposition with a target-to-substrate distance of 11 cm and rotation of the substrate holder.

The film thickness was measured by taking cross-sectional images of the films in a LEO 1550 Gemini SEM. The thickness was measured at three places on the film. The average of these measurements were calculated and used as the film thickness to minimize the measurement errors. It should be noted that there is a charge build-up on insulating films...
in the SEM which results in a low image quality making the thickness measurements uncertain and microstructural investigations difficult.

The NRA and ERDA measurements were made at the ion beam center at Forschungszentrum Dresden-Rossendorf outside Dresden, Germany. In the NRA measurements, $^{15}$N ions from a gas source were accelerated in a 5 MV tandem accelerator to energies ranging from 6.4 MeV to 7.2 MeV. The resulting $\gamma$-rays were detected by a $\gamma$-ray detector. The 5 MV tandem accelerator was also used in the ERDA measurements but with Cl$^{7+}$ ions at a total ion energy of 35 MeV. The main detector was a Bragg ionization chamber while the hydrogen was detected in a solid state detector with an Al stopping foil. The results were analyzed using the program NDF[18] where the ERDA spectra and the spectra of the front scattered Cl ions were fitted simultaneously.
6 Results and Discussion
The work on this thesis can be divided into two phases; film deposition and process analysis, and film characterization.

6.1 Film Deposition
Ten films were deposited with different background pressures and different F$_2$ partial pressures as shown below in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O pp:$^1$</td>
<td>0</td>
<td>1·10^{-5}</td>
<td>1·10^{-5}</td>
<td>1·10^{-5}</td>
<td>1·10^{-5}</td>
<td>1·10^{-5}</td>
<td>1·10^{-5}</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$_2$ pp:</td>
<td>0</td>
<td>2.5·10^{-6}</td>
<td>5·10^{-6}</td>
<td>1·10^{-5}</td>
<td>2·10^{-5}</td>
<td>3·10^{-5}</td>
<td>4·10^{-5}</td>
<td>5·10^{-5}</td>
<td>5·10^{-5}</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Deposition conditions for the samples, partial pressures given in Torr.

6.2 Mass Spectrometry
Mass spectrometry measurements were performed during depositions to evaluate the influence of F$_2$ on the H$_2$O and O$_2$ concentrations.

Figure 3 shows the O$_2$ concentration for depositions with different F$_2$ concentrations. It shows that the O$_2$ concentration is higher for higher F$_2$ concentrations with the exception for the depositions with F$_2$ partial pressures of 5·10^{-6} and 2.5·10^{-6} Torr.

The H$_2$O partial pressures plotted in Figure 4 shows the same behavior during all depositions, a large decrease in H$_2$O vapor concentration during the first hour of the deposition.

---

$^1$ pp = partial pressure
deposition after which the H\textsubscript{2}O concentrations stabilize. The decrease can probably be attributed to gettering of the H\textsubscript{2}O to the sample and the chamber walls by sputtered species. The H\textsubscript{2}O pressure stabilizes since the H\textsubscript{2}O vapor influx to the system is constant while the pumping speed essentially is increased due to gettering, a new lower stable H\textsubscript{2}O partial pressure will therefore be established. However, while an influence by F\textsubscript{2} on the O\textsubscript{2} partial pressure can be observed no clear F\textsubscript{2} influence on the H\textsubscript{2}O vapor concentrations can be observed while. Eq. 1 explains the higher O\textsubscript{2} partial pressure with higher F\textsubscript{2} partial pressures but does not explain why no such trend can be observed in the H\textsubscript{2}O partial pressures. However, much of the H\textsubscript{2}O in the chamber is condensed on the chamber walls and is therefore not measured by the mass spectrometer. A lot of H\textsubscript{2}O will be condensed on the chamber walls at these partial pressures making reactions according to Eq. 1 much more probable on the chamber walls than in the vacuum.

\[
2H_2O + 2F_2 \rightarrow O_2 + 4HF \quad \text{(Eq. 1)}
\]

The increase in the O\textsubscript{2} concentration with increasing F\textsubscript{2} concentrations can therefore be attributed to the reaction between H\textsubscript{2}O and F\textsubscript{2} on the chamber walls.

![Graph showing H\textsubscript{2}O partial pressures versus elapsed deposition time for different F\textsubscript{2} partial pressures.](image)

**Figure 4:** H\textsubscript{2}O partial pressures versus elapsed deposition time for different F\textsubscript{2} partial pressures.

### 6.3 Film Characterization

The deposited films were analyzed to find the influence of F\textsubscript{2} on the deposition rate, film composition and crystal structure. The techniques used are described briefly in chapter 4.
6.3.1 Scanning Electron Microscopy

Scanning electron microscopy was used to measure the thickness of the deposited films which were used to calculate the deposition rate, shown in Table 2, and to study the microstructure of the films.

All films have a similar microstructure with Figure 5 and Figure 6 shown two typical films. There is no grain formation, as can be expected from alumina deposited at room-temperature. The films are also uniform without voids and cracks. The light halo that can be seen above the films, to the right of the films, in Figure 5 and Figure 6 is due to charge build-up on the film surface.

The deposition rate of the films deposition with F\textsubscript{2} in an atmosphere with H\textsubscript{2}O shows a linear decrease, see Figure 7, with higher F\textsubscript{2} partial pressures. The decrease in deposition rate can be explained by etching of the films by fluorine during the deposition with a mechanism similar to that of reactive ion etching (RIE) described in [19] and [20]. The sputtering of substrate required for the etching must be done by other particles than Ar\textsuperscript{+} ions since the substrate potential was floating. Energetic O\textsuperscript{-} ions have been suggested to have a resputtering effect on films[3]. This effect would be increased in this case since the sputter yield is higher for AlF\textsubscript{3} and AlO\textsubscript{x}F\textsubscript{y} than for Al\textsubscript{2}O\textsubscript{3}[20].

<table>
<thead>
<tr>
<th>Sample</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Film thickness (nm):</td>
<td>228</td>
<td>336</td>
<td>258</td>
<td>253</td>
<td>219</td>
<td>216</td>
<td>184</td>
<td>159</td>
<td>153</td>
<td>82</td>
</tr>
<tr>
<td>Deposition rate (nm/min):</td>
<td>0.95</td>
<td>1.12</td>
<td>1.08</td>
<td>1.05</td>
<td>0.91</td>
<td>0.90</td>
<td>0.77</td>
<td>0.66</td>
<td>0.64</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 2: Film thicknesses and deposition rates.

The samples deposited in an atmosphere containing H\textsubscript{2}O had a higher deposition rate than the samples deposited in a clean chamber. This is contrary to the results Wallin et al. [3] got when depositing crystalline alumina films with an H\textsubscript{2}O partial pressure of 1 mPa at a substrate temperature of 500 °C. These films had a significantly lower deposition rate.
than the samples deposited in a clean chamber. The difference in deposition rates can most likely be attributed to a lower density of the films deposited in an H$_2$O containing atmosphere during this work. The lower density of these films can be explained by incorporation of hydrogen in the films and the formation of aluminum hydroxides since the sample deposited in UHV have a hydrogen content of 0.2% and the samples deposited in an H$_2$O containing atmosphere have a hydrogen content 9.5% while all the films in [3] had a hydrogen content lower than 0.7%.

Sample 10, deposited with an F$_2$ partial pressure of $5 \cdot 10^{-5}$ Torr in a clean chamber, shows the lowest deposition rate, about half of that of sample 9, deposited with the same F$_2$ partial pressure and $1 \cdot 10^{-5}$ Torr of H$_2$O. This indicates that the etch rate on sample 10 is higher than the etch rate on sample 9. The lower etch rate on sample 9 can most likely be attributed to HF formation between F$_2$ and hydrogen in the film since, according to Zhang et al. [21], fluorine breaks the O-H bonds in the hydroxyl groups on alumina surfaces and bonds the hydrogen before it breaks the Al-O bonds and bond to the aluminum.

![Figure 7: Deposition rates as a function of F$_2$ partial pressure](image)

**6.3.2 Nuclear Reaction Analysis**

Figure 8 shows hydrogen depth profiles acquired from the NRA measurements. The depth profiles show that the hydrogen concentrations are stable within the margin of error of the measurement through most films. The three films where the hydrogen concentrations are not stable are showing a pile-up of hydrogen near the film-substrate interface. The average hydrogen concentrations, shown in Figure 9, show a small increase in hydrogen concentrations from 9.5 at.% to 11 at.% for samples 3 and 4 when increasing the F2 partial pressure from 0 to $5 \cdot 10^{-6}$ Torr with a background of $1 \cdot 10^{-5}$ Torr H$_2$O. The average hydrogen concentration then decreases for increasing F2 partial pressure until it levels out at about 3 at.% at F2 partial pressures above $2 \cdot 10^{-5}$ Torr.
Figure 8 shows that the hydrogen depth profiles are similar for samples 3, 4 and 9 that were deposited on three consecutive days. The hydrogen content is increasing with depth implying that the cause of this behavior is the same for these samples. A cause of this behavior can be difficulties in keeping the same H₂O partial pressure between depositions. Other explanations for this behavior can be connected to contamination from the gas connection for the Ar/F₂ gas mixture where the gas pipe is long and therefore to hard get clean.

A reason for the leveling out of the hydrogen concentration for the films deposited with a F₂ partial pressure above \(2 \cdot 10^{-5}\) Torr can, again, be difficulties keeping the same H₂O partial pressure between depositions. Another plausible reason might be that the distance between hydroxyl groups at the surface is large. This means that the fluorine is more likely to find and break Al-O bonds than O-H bonds therefore lowering the rate of hydrogen removal while the etch rate of the film increases.

NRA also provides a way of measuring the stability of the hydrogen bonds by measuring the variation of the hydrogen concentration as a function of bombardment time. Bonded hydrogen is detected if the concentration is stable, otherwise the hydrogen present is not bonded or in H₂O molecules incorporated in the material. The hydrogen concentrations were stable for all samples indicating that the hydrogen is indeed bonded.
6.3.3 Elastic Recoil Detection Analysis

It is possible to do depth profiles of the films with ERDA however only mean values of the atomic concentrations in the films are shown here because no or only very small variations in atomic concentrations with depth were found. The ERDA measurements, in Table 3, show that the reference sample deposited in a clean chamber, sample 1, have a stoichiometric composition (stoichiometric Al$_2$O$_3$ is 40% Al and 60% O).

In sample 2 there is an apparent substitution of aluminum for hydrogen while the oxygen concentrations stays the same as in sample 1. The incorporation of hydrogen is due to the formation of aluminum hydroxides, with the main aluminum hydroxides being Al(OH)$_3$ and AlOOH[5], in the film when H$_2$O is present during the deposition.

The hydrogen concentration increases when low amounts of F$_2$ are introduced during the deposition of sample 3 and 4, as was also shown by the NRA measurements, while the aluminum concentration stays the same. The oxygen concentration is lower in these films due to substitution of oxygen with fluorine as well as the increased hydrogen concentrations. The hydrogen concentration decreases even more when the increase of the F$_2$ partial pressure during the depositions is continued. First to 6.4 at.% for sample 5 and about 3 at.% in samples 6, 7 and 8. The fluorine concentrations increase considerably for each increment in F$_2$ partial pressure as the fluorine substitutes not only hydrogen in the film but also oxygen.

The aluminum concentration increases from ~31 at.% for samples 2-4 to ~34 at.% for samples 6-9 deposited at higher F$_2$ partial pressures, see Figure 10, while the hydrogen concentration decreases by an almost equal amount. It is possible to conclude that this decrease in the hydrogen concentration is not because of substitution by fluorine or

![Figure 9: Average hydrogen concentrations versus F$_2$ partial pressure.](image)
oxygen by studying the combined fluorine and oxygen concentrations does not increase as much as the hydrogen concentration decreases.

This is the desired substitution of hydrogen with aluminum assisted by fluorine. A likely mechanism for this substitution is that the hydrogen in an aluminum hydroxide group is bound by fluorine forming gaseous hydrogen fluoride followed by the formation of alumina, aluminum or AIOF from the remains of the aluminum hydroxide and additional aluminum and/or oxygen because formation of aluminum fluorides would not lead an increase in the aluminum concentration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (g/cm³)</th>
<th>Al (at %)</th>
<th>F (at %)</th>
<th>O (at %)</th>
<th>H (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.03</td>
<td>40.3</td>
<td>0.1</td>
<td>59.5</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>2.8</td>
<td>30.7</td>
<td>0</td>
<td>59.5</td>
<td>9.8</td>
</tr>
<tr>
<td>3</td>
<td>2.7</td>
<td>30.9</td>
<td>3.74</td>
<td>55</td>
<td>10.36</td>
</tr>
<tr>
<td>4</td>
<td>2.6</td>
<td>30.7</td>
<td>5.82</td>
<td>52.2</td>
<td>11.28</td>
</tr>
<tr>
<td>5</td>
<td>2.9</td>
<td>32</td>
<td>19.3</td>
<td>42.3</td>
<td>6.4</td>
</tr>
<tr>
<td>6</td>
<td>2.4</td>
<td>34.4</td>
<td>33.8</td>
<td>28.5</td>
<td>3.3</td>
</tr>
<tr>
<td>7</td>
<td>2.6</td>
<td>34.3</td>
<td>38.3</td>
<td>24.1</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>2.7</td>
<td>34</td>
<td>42.4</td>
<td>20.6</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>2.2</td>
<td>33.9</td>
<td>46</td>
<td>17.5</td>
<td>2.6</td>
</tr>
<tr>
<td>10</td>
<td>3.4</td>
<td>38</td>
<td>39.8</td>
<td>21.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 3: ERDA results. The F concentration given for sample 1 is the detection limit and does not represent any actual F in the sample.
Figure 10: Elemental composition of samples 3-9.

It is also possible to calculate the thickness or density of the films using the ERDA results if the other parameter is known by using the formula:

$$t = \frac{N_M \cdot < M_Z >}{\rho \cdot N_A} \quad \text{(Eq. 2)}$$

where $t$ is the thickness in cm, $N_M$ is the areal density in at/cm$^2$, $< M_Z > = \sum f_Z \cdot M_Z$ is the average atomic mass in g/mol, $f_Z$ is the atomic fraction for element $Z$, $M_Z$ is the atomic weight for element $Z$, $\rho$ is the density in g/cm$^3$ and $N_A$ is Avogadro's number with the unit mol$^{-1}$. The results are shown in Figure 11. The large variations in density are most likely due to errors in the film thickness measurements. However it is possible to see that the measured densities of the films deposited with an H$_2$O background, samples 2-9, all have a lower density than the films deposited in a clean chamber. This is consistent with the density of bulk materials where the aluminum hydroxides, 2.45 g/cm$^3$ for crystalline Al(OH)$_3$, 3.08 g/cm$^3$ for crystalline AlOOH[5] and 3.1 g/cm$^3$ for crystalline AlF$_3$[22], have a lower density than amorphous alumina, 3.5 g/cm$^3$[23].
Figure 11: The film density as a function of F$_2$ partial pressure during the deposition.

6.3.4 X-Ray Diffraction

All films were deposited at room temperature where formation of crystalline alumina is not possible. However, since synthesis of aluminum fluoride thin films by sputter deposition have not been investigated thoroughly room temperature formation of crystalline aluminum fluoride might be possible. The films deposited with the highest F$_2$ partial pressure, $5 \cdot 10^{-5}$ Torr, were therefore investigated with XRD. The resulting diffractogram is shown in Figure 12. There are no clear peaks in the diffractogram meaning that the sample is X-ray amorphous. There is, however, an indication of a peak at $2\theta = 38.47$, which coincides with the aluminum(111) peak[24], possibly indicating the presence of small crystalline aluminum grains.
Figure 12: Diffractogram of the sample sputtered with $5 \cdot 10^{-5}$ Torr $F_2$ and $1 \cdot 10^{-5}$ Torr $H_2O$. The vertical lines show the positions of the two main peaks for Al[24].
7 Conclusions
Depositions of alumina thin films have been made by RF-sputtering under simulated high vacuum conditions in the presence of F₂ to investigate if the introduction of F₂ decreases the hydrogen content in the films. It was found that the hydrogen content in the films is lowered from about 10 at. % in a film deposited without any F₂ in the chamber to about 3 at. % if the F₂ partial pressure is sufficiently high. This increases the aluminum concentration in the films by about 3 at.% by directly substituting hydrogen with aluminum. However, it was also found that over 20 at. % of fluorine had been introduced in the films when a lowering of the hydrogen content in the films could be seen.

Film thickness measurements showed that the deposition rates decreased with increasing F₂ partial pressures during the depositions which is attributed to etching of films by the fluorine. The densities of all films are lower than that of stoichiometric amorphous alumina this can be attributed to that the hydrogen incorporated in the films is bound in aluminum hydroxide groups and that the fluorine reacts with aluminum and forms aluminum fluoride both of which have a lower density than alumina.

Mass spectroscopy measurements during the depositions show that the F₂ reacts with H₂O on the chamber walls and substrates since the H₂O partial pressure is similar in all depositions. The reduction of the hydrogen content in the films therefore takes place in reactions between fluorine and hydrogen in H₂O adsorbed on the film surface or hydrogen in hydroxide groups on the film surface.
8 Future Work

The high amounts of fluorine incorporated must be lowered for this method to be of any practical use as a way to reduce hydrogen concentration in alumina films. One way of doing this could be to do the depositions at elevated substrate temperatures, as opposed to room temperature which was used for the depositions in this work. Watanabe et. al.[25] have found that fluorine desorbs from AlF₃ layers formed on Al₂O₃ at sample temperatures above ~350 °C and that AlF₂ desorbs temperatures above ~580 °C at a pressure of 1·10⁻⁸ Torr. Another way could be to use another reactive gas, for example chlorine, whose the aluminum compound have a lower vapor pressure than aluminum fluoride.

An added benefit of doing high temperature depositions is that it is possible to investigate if the addition of fluorine lowers the transition temperature for crystalline alumina phases as shown in [13] and [14]. Gaudon et. al. [26] shown that it is possible to form bulk Al₂O₃ by calcination of AlF₃ in the presence of dry air. It might therefore be possible to reduce the fluorine concentration in the films by introducing O₂ during the deposition.

A reduction on the fluorine incorporation in the films might also be achieved by sputter etching of the growing film since AlF₃ and AlOₓFᵧ have higher sputter yields than Al₂O₃[20]. However, this would almost certainly lead to very low deposition rates.
9 References


[24] JCPDS card no. 04-0787
