Plasma Oxidation
for
Magnetic Tunnel Junctions

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The cover shows a stack of sample boxes used in the research described in this thesis.

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Chapter 1

General Introduction

1.1 Storage using magnetism

In one of many stories, it is told that the “invisible force” now known as magnetism was named after the Cretan shepherd Magnés who discovered it around 900 B.C. when black stones in a field he crossed pulled on the iron nails in his sandals. It wasn’t until the third century B.C., however, that mankind developed the first application of this invisible force: when it was discovered that lodestone needles aligned themselves in the same north-south direction everywhere, the compass was born. Today, magnetism is used in many applications like generators of electricity, storage of information on tapes and read-heads for hard-disks.

More high-tech applications of magnetism have emerged in the last few decades, and it is remarkable that it is often used for storage purposes: a Tokamak is used to store (confine, actually) hot matter in the form of a plasma in order to make fusion processes possible, and a magnetic bottle finds applications in the safe storage of anti-matter, although for short times only. An emerging storage application of magnetism that is closer to private usage is Magnetic Random Access Memory or MRAM, to be used in computers for storage of digital information. As will be explained in the next section, MRAM has one specific advantage over current types of computer memory: MRAM is non-volatile. This means that, after writing information, no power is needed to keep the information practically forever. Flash Memory is the type of non-volatile memory that is currently used most often in, for instance, digital camera’s and portable USB memory devices (“memory keys”), but is far too slow to serve as the working memory of personal computers. MRAM has several advantageous aspects with respect to Flash memory: the read-out rate can be much higher, the lifetime is longer by several orders of magnitude and the storage density can be much higher [Das03]. Hence, MRAM has the advantages of (S)DRAM, the type of
working memory that is used in all computers today, and adds to it the non-volatility. Using MRAM implies a much lower power consumption, which is ideal for mobile applications as MP3-players and laptops. For personal computers, MRAM offers the possibility of “Instant-On” operation: a PC can be turned off and on again without the need for performing the complete boot-up sequence that can take several minutes.

The first prototype MRAM chips, with low information density and low operating frequency, have been demonstrated already [Teh00, Dur03, DeB04] and it is expected that they will be ready for production within a few years.

1.2 Magnetic tunnel junctions

The part of an MRAM chip that is responsible for the actual storage of one bit of information is a magnetoresistive device, for example a so-called Spin-Valve [Koo96] or a Magnetic Tunnel Junction, see for example [Teh00]. In this chapter we focus on the application of Magnetic Tunnel Junctions, or MTJs, in MRAM. In the next section the working and the typical characteristics of these devices will be explained.

1.2.1 Quantum mechanical tunneling

For macroscopic objects with kinetic energy $E_k$, the probability of passing a potential barrier with energy $E_b > E_k$ is zero for all reasonable timescales like the age of the universe. For nano-scale objects, for instance electrons, such a process has a finite probability; this process is called quantum mechanical tunneling, see for example [Gri95].

A tunneling device consists in general of two metallic electrodes, separated by an insulating barrier layer that can be modelled as a step potential, as shown in Fig. 1.1. If a voltage $V$ is applied over the electrodes (say, positive on the right), the tunnel current from the left to the right electrode that will run through the barrier depends first of all on the density of states of the left and right electrodes $D_l(E)$ and $D_r(E)$, respectively. Next, one must

![Figure 1.1: Schematic potential diagram of a tunnel barrier between two metallic electrodes. The gray areas represent filled states, the hatched area is the energy gap of the barrier layer, which has a height $\phi$ above the filled levels of the metal electrodes. A voltage $V$ is applied.](image-url)
1.2. Magnetic tunnel junctions

take into account the number of electrons available on the left side, which is a fraction of the density of states (denoted by \( f_l(E) \)), and the number of available empty states on the right, a fraction \( 1 - f_r(E + eV) \) of the density of states. Finally, the transmission probability, dependent on barrier properties like height and thickness must be taken into account in the form of the square of a matrix element \( |M|^2 \) [Gri95]. We obtain:

\[
J_{l\rightarrow r}(V) = \int_{-\infty}^{+\infty} D_l(E) \cdot D_r(E + eV) |M|^2 f(E) [1 - f(E + eV)] \, dE. \tag{1.1}
\]

Using the so-called WKB approximation, Simmons [Sim63] calculated the tunnel current for \( T = 0 \) K through an arbitrary barrier with an average height of \( \phi \) and thickness \( d \):

\[
J(V) = \frac{J_o}{d^2} \left( \phi - \frac{eV}{2} \right) \exp \left[ -Ad \sqrt{\phi - \frac{eV}{2}} \right] - \frac{J_o}{d^2} \left( \phi + \frac{eV}{2} \right) \exp \left[ -Ad \sqrt{\phi + \frac{eV}{2}} \right], \tag{1.2}
\]

where \( J \) is the tunnel current density per surface area, \( A = 4\pi \sqrt{2m_e^*/\hbar} \) and \( J_o = e/2\pi \hbar \) are constants and \( m_e^* \) is the electron effective mass. This formula was derived for \( T = 0 \) K; the tunneling current will increase with increasing temperature [LeC02b].

1.2.2 Spin-dependent tunneling

If the electrodes are magnetic metals, \textit{i.e.} Co, Fe, Ni, or their alloys, the density of states for spin-up electrons and spin-down electrons are in general not equal, resulting in different up- and down-currents through the barrier. In a simple model, Jullièere discusses this concept of Spin-dependent Tunneling [Jul75]. In this model it is assumed that the tunnel current is proportional to the density of states at the Fermi-level of each electrode. The energy bands for the two spin-directions in a ferromagnetic material are different, which results in different densities of states at the Fermi level for majority \( (N_{maj}) \) and minority \( (N_{min}) \) spin electrons. The \textit{spin polarization} \( P \) is defined as

\[
P = \frac{N_{maj} - N_{min}}{N_{maj} + N_{min}}. \tag{1.3}
\]

The value of the polarization depends on the electrode material. For instance, for pure Co the polarization is 42%, and for Co\textsubscript{50}Fe\textsubscript{50} \( P \) is about 55%.

The density of states in one electrode can now be altered by reversing the magnetization of the electrode, giving rise to two situations: a) the magnetizations of the electrodes are aligned \textit{parallel} and b) the magnetizations are
aligned anti-parallel. The total current through the barrier can be calculated for each situation:

\[ a) \quad I_{\parallel} \propto N_{maj}N_{maj} + N_{min}N_{min} = N_{maj}^2 + N_{min}^2 \]
\[ b) \quad I_{\perp} \propto N_{maj}N_{min} + N_{min}N_{maj} = 2N_{maj}N_{min} \quad (1.4) \]

It is obvious that, if \( N_{maj} \) and \( N_{min} \) are not equal, these two tunnel currents are unequal. A switch of the magnetization of one of the electrodes will thus result in a different current and hence a different resistance. A measure of the relative change in resistance, the tunneling magnetoresistance TMR, is defined as

\[ TMR = \frac{R_{\parallel} - R_{\perp}}{R_{\parallel}} = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel}} = \frac{2P_1P_2}{1 - P_1P_2}, \quad (1.5) \]

where \( P_1 \) and \( P_2 \) represent the polarization in electrode 1 and 2, respectively.

In the tunnel process, it is assumed that this spin-polarization is completely conserved. Theoretically, a junction consisting of two Co\(_{50}\)Fe\(_{50}\) electrodes will display a TMR of about 87%. However, it is noted that the (bulk) polarization mentioned above is not necessarily the same as the polarization of the tunneling electrons [Moo99], such that the theoretical value deviates from experiments.

### 1.2.3 Switching

So far, it was just assumed that the two magnetic layers could be “set” independently, creating parallel and anti-parallel situations at will. In an applied field, both layers prefer to align themselves along the field lines. In order to make sure that an antiparallel situation can be achieved, one of the layers can be “pinned”. In practice, this “pinning” is done in several ways [LeC02b], for example by choosing two different electrode materials with different coercivity, or by adding an exchange bias layer. Such a layer consists of an anti-ferromagnetic layer that interacts with the magnetic electrode it is adjacent to, thereby artificially shifting the hysteresis loop of that electrode to a higher value. The behavior of such an exchange-biased junction when an applied field is swept from positive to negative fields and back is shown schematically in Fig. 1.2. The magnetization loops of the two electrodes \( M_1 \) and \( M_2 \), are also shown. \( M_2 \) is exchange biased to a negative field. This results in a resistance that changes with the applied magnetic field: when the layers are parallel, the resistance is low, when the two layers are anti-parallel, the resistance is high.

### 1.2.4 The magnetic tunnel junction structure

A schematic picture of a possible realization of a magnetic tunnel junction is shown in Fig. 1.3. On a substrate, the bottom electrode, including the
Figure 1.2: Individual magnetization curves of two electrodes 1 and 2 as the field is swept from positive to negative and back. Electrode 2 is exchange biased to a negative coercive field. The resulting resistance is shown in the bottom plot.

exchange bias layer, is grown. The typical thicknesses of both layers are 3 to 15 nm. Then the barrier layer is grown, covering the bottom electrodes. Finally, the top electrode is grown. Not shown in the picture for reasons of clarity are the buffer layers which are usually grown on the substrate to improve the growth of the subsequent layers, and a capping layer that is deposited on the top electrode in order to prevent oxidation [LeC02b].

The insulating layer, which is most often Al₂O₃, as in this research, can be created by two methods. The first method consists of the deposition of a thin aluminum layer and subsequent oxidation of the layer. The oxidation can be done “naturally”, in an oxygen atmosphere, or accelerated, by using a plasma for example. The second method involves direct deposition of Al₂O₃, for instance by reactive sputtering or by Atomic Layer Deposition.

Figure 1.3: A basic MTJ structure: the bottom electrode, including an exchange bias layer, lies on a substrate. On top of that an insulating layer (shaded area), and finally the top electrode. The resistance is measured over two electrodes; the tunneling area A is indicated by the hatched square.
Chapter 1. General Introduction

The tunneling barrier (including its interfaces with the electrodes) is the most crucial part in any magnetic tunnel junction. For a proper operation of the tunnel junction, the following issues must be taken care of:

- The barrier must be homogeneous, without pinholes (paths of higher conduction) or impurities that will cause large parasitic, unpolarized currents parallel to the polarized tunnel current, decreasing the TMR.

- The barrier must be smooth. Some roughness of the barrier thickness can cause inhomogeneous currents through the layer that can lead to very local heating and breakdown of the barrier, creating shorts.

- Roughness of the barrier can cause a magnetic coupling between the two electrodes [vdH98], which results in the situation that the layers do not switch independently and an anti-parallel state cannot be achieved anymore.

The structuring of the electrodes and barrier layer can be done by growing through shadow masks [LeC02b], or by lithographic patterning afterwards [Kol04a]. The tunneling area is indicated in Fig. 1.3 by the hatched square. Additional to the tunnel barrier height and thickness, the area determines the resistance of the tunnel junction as well. Usually, the product of the resistance and the area, $R_A$, which is the “specific resistance”, gives an indication of the barrier properties making it possible to compare junctions of different sizes.

We will now return to the application of magnetic tunnel junctions in MRAM: when an MTJ is applied as a memory element, the parallel alignment of the magnetization of the two electrodes, i.e. a low tunnel resistance, can now be defined as a logical “1”, and the anti-parallel alignment as a logical “0”. Since the electrode materials are made of ferromagnetic metal, i.e. permanent magnetic material, the relative orientation of the magnetizations will not change in time.

In an MTJ embedded within an MRAM chip, it must be possible to switch the magnetization of the top layer in order to write a logical “1” or “0”. Basically, this can be done by running a current through the electrodes in order to create a magnetic field that is strong enough to switch the magnetization of the top layer to one direction, but not strong enough to switch the magnetization of the bottom electrode. Running the current in the other direction will result in the other magnetization direction of the top electrode. The remanent magnetization of the ferromagnetic electrodes ensures that the relative alignment of the electrodes is kept when the write-current is turned off.

Summarizing, we have now a non-volatile memory cell which can store one bit of information without the necessity of refreshment to retain the state.
it is in. For more in-depth information on MRAM operation the reader is referred to the work of Prinz [Pri99] and the thesis of Das [Das03]. Next, it is necessary to investigate the demands on tunnel barriers before they can be applied in high density MRAM.

1.3 Demands on tunnel barriers for high density MRAM: Resistance vs TMR

The first MRAM demonstration chips have been shown to work [Teh00, Dur03, DeB04], although with a limited storage capacity of maximally 16 Mbit. As the demands for the storage density and operating frequency are increased, the area of the junctions must decrease [Das03]. As mentioned in the previous section, this implies that the resistance will increase if the other barrier properties (thickness, height) are kept the same. If the resistance increases, the noise will increase (as will be shown below) and the signal-to-noise ratio (SNR) becomes an important issue that will impose limitations on the resistance and the TMR of the junctions, as will be explained in this section.

Assume that the noise is mostly due to thermal or Johnson noise that appears in all resistors\(^1\) [Joh28]. The voltage level can be calculated as [Dau97]:

\[
V_n = F \ast \sqrt{4kT R \over \tau}
\]

where \(R\) is the resistance, \(T\) is the temperature and \(\tau\) is the read-out time, or the inverse of the operation frequency. \(F\) is a noise factor, which is ideally 1 [Dau97]. The theoretical lowest value of 1 is used here. The resistance of a junction depends of course on the \(R \times A\) product and on the area. For the MRAM to be able to compete with state-of-the-art DDR SDRAM, which uses 80 nm technology [Yeo04], we can take \(50 \times 50\) nm\(^2\) and, a little further in the future, \(20 \times 20\) nm\(^2\) to be the junction area. The operating frequency for high-end devices will be of the order of 500 MHz, and increasing to 1 GHz in the future\(^2\), hence \(\tau\) will range from 2 ns to 1 ns. The operating temperature of the device will be somewhat above room temperature, at maximum 50°C, as is common in present-day integrated circuits for personal computers.

For a low failure rate, the signal voltage \(V_s\) must be at least 20 times higher than the noise voltage \(V_n\) as is commonly accepted in electronics [Dau97]. The signal voltage can be estimated to be the TMR value times

\^1\(It\) is noted that shot noise is important for low-resistance MTJs as well, but is not necessary for the discussion here [Kla04].

\^2\DDR memory in the latest high-end computers already operates at frequencies around 400 to 800 MHz.
Figure 1.4: The TMR (at room temperature) vs the R×A product of junctions made by thermal oxidation (open circles) and plasma oxidation (closed squares) reported in literature. The lines indicate the limits for a SNR of 20, as calculated in Eq. 1.8. The arrow indicates the improvement that is necessary for junctions to match the demands on the signal-to-noise ratio for application in high-density MRAM.

the operating voltage of the MTJ, which is usually about 0.1 V\(^3\). A relation between the R×A product and minimal TMR can now be calculated:

\[
V_n < \frac{TMR \times 0.1 \text{ V}}{20}, \quad (1.7)
\]

\[
TMR(\%) > 4.22 \sqrt{R \times A(\Omega \mu \text{m}^2)} \quad (1.8)
\]

This curve is shown together with data on MTJs found in literature in Fig. 1.4. It can be seen that already several junctions have been reported that have a sufficiently low R×A product and sufficiently high TMR for application in MRAM devices. The barriers of most of these devices have been created by thermal oxidation of a thin aluminum layer, which is a very slow process, whereas for production lines a high throughput is preferred. Plasma oxidation is in general a much faster process which on the average produces high TMR junctions, but tends to result in high values of the R×A product as can be seen in Fig. 1.5, where the resistance-area product is plotted versus the deposited Al thickness. The difference in resistance

\(^3\)If the TMR of a device is 20%, the signal voltage will be approximately 20 mV. Also note that the TMR decreases with increasing voltage [LeC02b], which is not taken into account in this discussion.
1.3. Demands on tunnel barriers for high density MRAM

between the oxidation processes may be due to a larger oxide thickness or different stoichiometry of the oxide. Therefore, more research is needed to decrease the areal resistivity, $R_A$, of plasma-oxidized tunnel junctions, as indicated by the arrows in Fig. 1.4 and Fig. 1.5. In order to do so, a thorough knowledge of the plasma-oxidation process is necessary, which can be done by studying the dynamics of the oxidation process in combination with plasma characteristics.

![Figure 1.5: The $R_A$ product (at room temperature) vs the deposited aluminum thickness of junctions made by thermal oxidation and plasma oxidation.](image-url)
1.4 This Thesis

The research that has been done so far on the oxidation of ultra thin layers of aluminum using a plasma has been merely empirical (see for example [Kui01a]). A good comprehension of the process can give good directions for more improvements. Therefore, in this thesis, the plasma oxidation process is studied by comparing surface science measurements and plasma characterization.

First, a review on oxidation processes used for MTJs and barrier issues is given in chapter 2 in order to establish what has been done on this subject. Then a theoretical basis is formed of oxidation models and plasma characteristics in chapter 3 in order to be able to discuss the possible role of a plasma in oxidation models, as well as the influence of the very small aluminum thicknesses used in typical magnetic tunnel junctions.

The measurement techniques that are used in this thesis include, among others, XPS, LEIS, Langmuir probes, TALIF and actinometry, and will be discussed in chapter 4. Furthermore, a differential ellipsometer is developed for in-situ characterization and allows for real-time observation of the oxidation process, as will be outlined in chapter 5.

The experiments performed are divided in two parts: in chapter 6, the oxidation dynamics are studied without taking the physics of the plasma into consideration. In chapter 7, the influence of a plasma is investigated and results are compared to the theories introduced in chapter 3. Using the available theory and measurements, a novel model that describes the plasma oxidation process is developed and confirmed by measurements.

Chapter 8 is dedicated to a promising alternative method of barrier growth, namely Atomic Layer Deposition (ALD). The technique is outlined and measurements performed to characterize junctions made by ALD are discussed.
Chapter 2

Reported Results On The Oxidation of Aluminum for MTJs

2.1 Introduction

After the first junctions with a high magnetoresistance of 12% were made by Moodera et al. [Moo95], a lot of efforts have been made in the search for MTJs with better properties like high TMR, low R×A product and high breakdown strength. To this end, a wide variety of oxidation techniques has been applied, including plasma oxidation, thermal oxidation, ion beam oxidation and UV-light assisted oxidation. In Fig. 2.1, results found in literature for junctions made by these techniques are shown.\(^1\)

With very few exceptions, it is clear that plasma oxidation, indicated by the solid squares within the large oval, distinguishes itself from all other techniques by the highest values of TMR, but also with a characteristically high value of the R×A product. Thermally oxidized junctions, grouped mostly in the smaller oval, have in general a low R×A product but also a lower magnetoresistance. The other techniques, which were tried for their potential of making junctions with both a high TMR and low R×A product, are situated between those extremes.

Even with such a variety of techniques it currently appears to be almost impossible to enter the upper-left part (low R×A product, high TMR) of Fig. 2.1. It is suggested by Boeve et al. [Boe01] that inhomogeneities in the barrier cause a lower TMR and R×A product. The density or relative significance of the inhomogeneities might intrinsically depend on the thickness of the aluminum oxide layer, resulting in the observed “limit” in Fig. 2.1.

\(^1\)All results reported in this chapter have been measured at room temperature, since this is likely to be the working temperature of MTJ devices in applications.
Chapter 2. Reported Results On The Oxidation of Aluminum for MTJs

Before discussing the results reported in literature in more detail, the reader must bear in mind the following issues:

- The TMR depends on the polarization of the electrodes, which is material-specific (see section 1.2.2). In the literature, a wide range of electrode materials is used, each chosen for a particular goal. For instance, Co$_x$Fe$_{1-x}$ and Ni$_y$Fe$_{1-y}$ are most commonly applied in actual devices because of their high values of polarization and should therefore, in the simple model of Jullière, result in junctions with the highest values of TMR (see section 1.2). However, in fundamental research (see for example [LeC02a]) often pure Co is preferred because it is a more basic material of which more knowledge is available, like structural data and the density of states.

- A second, more practical possible difference stems from the reasonable assumption that the structure of the unoxidized aluminum layer influences the oxidation process and therefore the quality of the resulting barrier. The oxide growth can easily be imagined to be different from planar oxidation if the aluminum layer has a grain-like structure. Such a growth mode is intrinsically induced by the layer on which

![Figure 2.1: TMR versus the RxA product (at room temperature) of junctions made by various barrier production techniques. The big and small circles indicate the group of plasma and thermally oxidized junctions, respectively. For the underlying data including references, see appendix A.](image-url)
the aluminum is grown and can vary with the bottom layer material and with the deposition technique. For example, Ando and coworkers have shown by simple AFM measurements that the roughness of the aluminum can be reduced with 80% by replacing the aluminum buffer layer under the bottom electrode by Pt [And00]. The deposition parameters and characteristics of the deposition facility can play a huge role. For instance, a small amount of surface contamination can induce a different mode of growth of the aluminum layer. Fujikata et al. report a considerable improvement of TMR in junctions with an intentionally contaminated Ta buffer layer in their junctions [Fuj01].

- Finally, in the case of plasma oxidation and UV-oxidation, the exact lay-out and operation of the oxidation set-up are never fully given in literature, which makes it difficult to compare results.

Because of the issues mentioned here, any comparison between oxidation techniques found in literature should be considered with great care. This chapter will give an overview of the different techniques which are used, but the reader should keep in mind that a higher TMR and/or a lower $R \times A$ product are not necessarily the result of a better or more innovative oxidation technique.

2.2 Oxidation processes used for MTJs

2.2.1 Plasma oxidation

Plasma oxidation is currently the most common method of producing aluminum oxide for MTJs with the highest values of TMR. As mentioned above, Moodera was the first to reproducibly produce MTJs using plasma oxidation, and many groups have followed using numerous varieties of plasma oxidation. A DC glow plasma, as is used in this thesis, is easy to set up and is therefore most commonly applied. An Inductively Coupled Plasma (ICP) is generated without electrodes [And02, Son03], which means that there is no contamination by sputtering of electrode material and is therefore thought to produce less impurities in the tunnel barrier\(^2\). Plasmas generated by radio-frequency or microwave radiation have been successful in plasma oxidation of silicon and are therefore also applied for aluminum oxidation, for example by Yoon et al. [Yoo01] and Sun and Freitas et al. [Sun99].

As mentioned before, plasma oxidation is very fast as compared to many other oxidation methods. For example, Park et al. optimally oxidize 1.8 nm

\(^2\)To our knowledge, there is no evidence reported in literature that impurities in the barrier due to plasma-electrode-sputtering are causing a degradation of MTJ properties.
Chapter 2. Reported Results On The Oxidation of Aluminum for MTJs

of aluminum in approximately 40 seconds [Par01b], and Kuiper and coworkers need only 20 seconds of plasma oxidation to optimally oxidize 1.5 nm of aluminum [Kui01a].

Variations in plasma pressure and plasma composition can improve results. Following the success of a krypton-oxygen mixture (97%:3%) in silicon oxidation [Sek01], junctions with a TMR of 59% have been obtained by Tsunoda et al. [Tsu02]. No suggestions as to why the krypton improves results with respect to argon or helium were given.

The maximum reported value of magnetoresistance is currently 70.4%, produced by Wang et al. [Wan04]. However, the resistance of these junctions is very high, about 20 MΩμm², and therefore practically not applicable in devices.

Tunnel junctions made by plasma oxidation with the lowest resistance-area product (R×A product) were made by Ando et al. [And00]. The barrier layer in their tunnel junctions was made by ICP oxidation of 0.8 nm Al. After annealing of the complete junction stack the junctions display an R×A product of only 230 Ωμm² and a high TMR of 31%.

Tehrani et al. [Teh00] were the first to report an actual integrated MRAM chip using MTJs. The 512 bit chip employed junctions of 0.6 × 1.2 μm² area with an R×A product of 11 kΩμm², while the magnetoresistance is 31%. The oxidation was performed using an RF plasma. A larger integrated MRAM chip is the Motorola 4 Mbit chip by Durlam and Tehrani et al. [Dur03]. Their MTJs [Teh03] have 45% TMR and an R×A product of 10 kΩμm². The area of the integrated MTJs is 1.55 μm². The access times of the memory cells reported on are 35 ns, corresponding to an operating frequency of about 30 MHz. The largest MRAM chip to date is the IBM 16 Mbit chip, by DeBrosse et al. [DeB04]. As mentioned in section 1.3, for higher density and higher operating frequency, smaller junctions are necessary, emphasizing the need for smaller resistance-area products.

2.2.2 Thermal and natural oxidation

In order to create junctions with lower specific resistances, thinner barriers have to be made. For the oxidation of Al layers of 1 nm or less, plasma oxidation is thought to be too rough and not sufficiently controllable, possibly resulting in damage to the bottom electrode. Therefore, for very thin layers often natural or thermal oxidation is chosen. For oxidation in an oxygen atmosphere at room temperature normally the term natural oxidation is used, whereas thermal oxidation refers to oxidation in an oxygen atmosphere where the sample is usually but not necessarily at an elevated temperature (above 50°C). For most junctions reported in literature, oxidation at room temperature is used.

Tsuge and Matsuda et al. were the first to use pure natural oxidation
for magnetic tunnel junctions [Tsu97, Mat99]. A TMR of 13% was found with an R×A product of only 1.5 kΩμm². The barrier was made by exposure of 2 nm Al to 0.27 bar of pure oxygen for one hour. The fact that a barrier made from an initial 2 nm Al results in an R×A product that is three orders of magnitude lower than plasma oxidized junctions starting with the same initial Al thickness (see Fig. 1.5), suggests that the barrier has an inhomogeneous thickness and the tunneling current runs through the thinnest parts of the barrier. The fact that the TMR is low is probably due to unoxidized aluminum. This suggests that the oxidation in this case is more inhomogeneous.

Natural oxidation is a slow process if the aluminum layer is thicker than 0.5 nm. For instance, the optimal oxidation of 1 nm Al takes 15 hours at room temperature, as reported by Das et al. [Das03]. In order to reduce processing time, Das uses two cycles of deposition of Al and subsequent oxidation. The oxidation time resulting in optimum TMR is thereby reduced from 15 hours to 2 × 2 hours. An identical technique was used by Moon et al. [Moo02] who report MTJs with 30% TMR and only 140 Ωμm². Han et al. report on experiments with multiple cycles of sputter deposition and oxidation, and find a TMR of approximately 40% and an R×A product of 60 Ωμm². However, their determination of the TMR is probably flawed by geometrical enhancement, which is due to the large junction area in combination with the low resistance (see for example [vdV99]).

Currently, the R×A-record of MTJs is held by Wang, Freitas and Zhang et al. [Wan03] (see also [Zha02, Zha01, Zha03]) and is set to 8 Ωμm² while the junctions have a TMR of 22%, which is within the limits of the demands for proper MRAM functionality as mentioned in section 1.3, Fig. 1.4.

2.2.3 UV-light assisted oxidation

Recently, oxidation assisted by UV-light irradiation has been tried as a faster method of aluminum oxidation for MTJs, possibly combining the low R×A product of natural oxidation and a higher oxidation rate and higher TMR.

Girgis and Boeve et al. [Boe00, Gir00] were in 2000 the first to report results on MTJs made with UV-assisted oxidation. They oxidized the sputter deposited 1.3 nm Al layer for one hour in a high pressure oxygen atmosphere of 100 mbar, assisted by an in-situ ultraviolet lamp³. They find an R×A product of 60 kΩμm² and a MR of about 20%. Compared with their naturally oxidized junctions, UV-oxidation results in higher TMR but also higher R×A products. Their plasma-oxidized junctions, which are identical except for the oxidation method, give a higher TMR but similar R×A products.

³Further experimental details, for example the radiation power density, are not mentioned.
Later experiments resulted in junctions with a TMR of 10%, with a typical R×A product of 1 kΩμm² [Rot00].

Li et al. [Li02] prepared junctions by UV assisted oxidation of only 0.5 nm of Al, resulting in a few percent TMR but an R×A product as low as 3.2 Ωμm². By oxidation of 0.4 nm Al an R×A product of approximately 0.6 Ωμm² is found, which is the lowest R×A product reported so far. The TMR in these junctions has dropped to 2%. Li reports that these junctions are shorted by metallic interconnects (pinholes, see section 2.3.3) between the ferromagnetic layers.

2.2.4 Other oxidation processes

Oxidation using ozone

As ozone is a more reactive molecule than oxygen⁴, it is used, for example, as a disinfectant. The high reactivity suggests that using ozone for aluminum oxidation, shorter oxidation times with respect to natural oxidation are possible, and that possibly larger oxide thicknesses as compared to natural oxidation are reachable within reasonable oxidation times.

An oxygen-ozone mixture to oxidize aluminum for MTJs is used by, for instance, Park and coworkers [Par01b, Par02]. In a comparison between ozone and plasma oxidized junctions, Park reports slightly higher TMR values, 33%, for junctions oxidized by ozone, whereas the R×A product of ozone oxidized junctions is one order lower. The lowest R×A product reported are 10.5 kΩμm². The process is still very slow; 50 minutes of oxidation were necessary to produce the junction described here. Junctions made by thermal oxidation have TMR values close to this value of TMR (30%, [Moo02]), but with considerable lower R×A product of 140 Ωμm² [Moo02].

Ionized atom beam oxidation

Roos and Hillebrands et al. [Roo00a, Roo01] used an ionized oxygen atom beam of low energy (30-80 eV) to oxidize the aluminum. MTJs with a 22% TMR but a very high R×A product of 1 GΩμm² were produced.

Freitas et al. used an ion beam for the deposition of the layers and for the oxidation process as well. The ion beam was created by inserting a grid between a high-power (80 W) Ar/O₂ plasma and the sample and applying a voltage of 30 V over the grid, accelerating oxygen ions towards the sample. With this technique, junctions with a TMR of 40% and an R×A product of only 400 Ωμm² [Car99, Fre00] were created. The high quality is explained by the better layer-by-layer growth, as compared to sputter deposition which

⁴See the theory chapter, section 3.4.3
is used more commonly in literature. The oxidation times for optimal TMR are comparable to plasma oxidation, of the order of 60 seconds.

**Radical oxidation**

Shimazawa *et al.* [Shi00] reported on experiments with oxidation using a beam of oxygen radicals, arguing that this can be a low energetic and slower process compared to plasma oxidation, thus suitable for the oxidation of ultrathin Al$_2$O$_3$ layers. The radicals were produced by a microwave (electron cyclotron resonance, ECR). Junctions with $R \times A$-values of 350 $\Omega \mu m^2$, with a TMR of about 11% were created.

Kula *et al.* applied radical oxidation as well [Kul03], resulting in junctions that have a TMR of 40% and a minimal $R \times A$ product of only 2 k$\Omega \mu m^2$. In a comparison with natural and plasma oxidation, for radical oxidation a higher TMR was reported, as well as a medium $R \times A$ product in between thermal and plasma oxidized junctions. The possible advantage of radical oxidation over plasma oxidation might be the absence of more energetic particles such as ions (see section 3.4.7).

**Direct deposition of Al$_2$O$_3$**

As an alternative to oxidation processes, direct deposition of Al$_2$O$_3$ layers has been tried in various forms.

First of all, *reactive sputtering* has been applied to create Al$_2$O$_3$ layers. By sputtering aluminum in an argon atmosphere which contains a few percent oxygen, in principle a homogeneous and stoichiometric Al$_2$O$_3$ layer can be obtained as shown by Koski *et al.* [Kos99]. The roughness of thick films ($\approx 1$ $\mu m$) grown on pure Si was reported to be about 0.7 nm. Nasser *et al.* [Nas98] were the first to apply this technique for the production of MTJs. A TMR of 6% was found with an $R \times A$ product of 180 $M\Omega \mu m^2$. The low TMR and high $R \times A$ suggest that the bottom electrode is oxidized in the process. Chen *et al.* [Che00] tried to improve the method by preventing the oxidation of the bottom electrode by first depositing 0.7 nm of pure Al before adding 0.5 nm of reactively sputtered Al$_2$O$_3$. Since their method resembles plasma oxidation, the results were comparable to their plasma oxidation results, with a TMR of 18% and an $R \times A$ product of 1 $M\Omega \mu m^2$.

The second method of direct Al$_2$O$_3$ deposition that has been tried is *Atomic Layer Deposition* (ALD) although without success so far [Bub02]. In chapter 8 the ALD process is explained in more detail and some experiments using ALD which are performed together with Bubber and coworkers are described.
2.2.5 Summary

Summarizing, it is found that plasma oxidation generally results in a high $R \times A$ product, but also in high values of TMR (Fig. 2.1). Junctions with thermally oxidized barriers, however, show low $R \times A$ values but usually a low TMR as well. Furthermore, thermal oxidation is a slow process, enormously increasing the processing time of MRAM chips.

The other oxidation techniques that were mentioned here display junction properties in between thermal and plasma oxidation. Therefore, plasma oxidation and ion beam oxidation (which is a special form of plasma oxidation) seem to be the best candidates for use in the production process of MRAM, as soon as the process is adapted and optimized for ultrathin barrier layers resulting in low-$R \times A$ junctions.

2.3 Towards an ideal barrier

Irrespective of the oxidation method, the combination of initial Al-thickness and oxidation time has to be chosen such that the MTJ properties are optimal, usually a high TMR and a low $R \times A$ product as has been discussed in section 1.3. Furthermore, as already mentioned in the introduction (sec. 1.2.4), for optimum TMR, the barrier must be homogeneous, that is, the pinhole density in the barrier must be as small as possible [Oli04]. In the following sections, experiments on the optimization of the oxidation process will be outlined.

2.3.1 Research methods

A number of diagnostic tools to study the results of the oxidation process is available. The most widely used method is of course the magnetoresistance measurement [Moo97, Gil99, Sun99] since it is directly aimed at optimization of the final junction that is implemented in the application. Additionally, the determination of the breakdown voltage can give some indication of the quality of a junction: the larger the pinhole or defect density is, the lower the breakdown voltage is.

Other surface sensitive techniques that are often applied to study the chemical composition of the junction are X-ray Photo-electron Spectroscopy (XPS) [LeC00a], Auger Electron Spectroscopy (AES) [Roo02], Rutherford Backscattering Spectroscopy (RBS) [Gil99] and Electron Recoil Detection (ERD) [Gil00]. Transmission Electron Microscopy (TEM), used for instance by Boeve et al. [Boe01, Bru01] is used to characterize the growth of the films, giving important information on roughness of the barrier. An ac-impedance technique is applied by Gillies et al. [Gil00] in order to characterize the dielectric properties of the barrier layer. In combination with modelling,
2.3. Towards an ideal barrier

Figure 2.2: Various methods for creating samples with over- and under-oxidized barriers. a) Same Al thicknesses, range of oxidation times. b) Range of Al thicknesses (or wedge), single oxidation step. c) Oxidation by an inhomogeneous plasma.

information on the structure of the barrier can be extracted. Photoconductance measurements [Kol03] have been used to extract information on the barrier asymmetry, as will be discussed shortly below.

In order to study the effect of the oxidation process or just to find the optimum oxidation parameters, often a series of samples which are in various states of oxidation is produced. This is usually done in one of the following two ways: either by depositing a number of identical samples, oxidized with various oxidation times, like in Fig. 2.2a, or by depositing a series of samples with a range of Al thicknesses, all oxidized at once like in Fig. 2.2b.

From an application point of view, the first method is used to obtain the optimum oxidation time for a specified barrier thickness for a specific application. However, this is a time consuming experiment due to the number of oxidation steps, since each oxidation includes a long pump-down stage and possibly sample transport. The second method, making one batch of samples with a range of Al thicknesses, usually allows for more rapid experiments because only one oxidation step is necessary. The use of a wedge is even faster, see for example the work of LeClair and Smits et al. [LeC00a], and Song et al. [Son00].

In a third method, applied by Nowak et al. [Now00] and Song et al. [Son00], a series of samples with various states of oxidation is made by a single deposition and a single oxidation step in a plasma that is *not* uniform over the wafer, see Fig. 2.2c. The interpretation of the results in terms of oxidation conditions of this method is of course much more complicated because the changes in the plasma conditions over the wafer are unknown and difficult to estimate. Furthermore, the local plasma conditions of one spot on the wafer cannot easily be copied for the complete wafer.

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5 See for example [Sun99, Son00, Par02, Gil99, vdV99, Gil00, LeC00b, Teh00]
6 See for example [Son00, LeC00b, Teh00, Moo97, Boe01, Fre03]
7 A wedge is a film with a thickness that varies linearly over some distance.
Chapter 2. Reported Results On The Oxidation of Aluminum for MTJs

2.3.2 Over- and under-oxidation

In Fig. 2.3a the potential scheme of an ideal metal-insulator-metal tunnel junction is shown. The barrier is rectangular, and both interfaces electrodes are taken to be identical, for example Co.

In Fig. 2.3b the potential diagram of a junction is shown as it would look like in theory if the barrier is not oxidized completely. The bottom electrode is in this case formed by metallic, non-magnetic Al that is left over. The current through the barrier is now no longer spin-polarized, and, depending on the amount of metallic Al left, the magnetoresistance will rapidly decay to zero. LeClair et al. [LeC01] demonstrated this effect by adding small amounts of “non-magnetic impurities” like Cu at the interface: the addition of 1 monolayer of Cu at the interface between the bottom electrode and the barrier decreased the TMR by 60%.

Over-oxidation, depicted in Fig. 2.3c, results in an amount of cobalt-oxide. CoO and Co$_3$O$_4$ are known to scatter spins, thereby mixing the spin-up and spin-down currents [Moo99]. This results in a lower spin-polarization and therefore a lower TMR. Furthermore, the barrier is thicker than aimed for, resulting in an R×A product that is possibly too high for the specific application this junction was intended for.

Using the diagnostic techniques mentioned above, it was primarily established by several groups that an asymmetry in a junction with identical electrodes, which is easily observed in IV-curves and quantitatively determined by fitting with Simmons formula (Eq. 1.3), is accompanied by a low TMR. Correspondingly, the maximum TMR is found when the junction has a minimal asymmetry, see the work of Sun and Freitas [Sun99], Covington [Cov00] and Oepts [Oep01]. Both over- and under-oxidation cause this asymmetry by creating different electrode-barrier interfaces.

An asymmetry in the barrier height itself, like in figure 2.3d, is observed by Koller et al. [Kol03] in photoconductance measurements of complete junctions. Koller concludes that the barrier asymmetry probably results from
2.3. Towards an ideal barrier

Figure 2.4: Creation and use of an oxygen reservoir. After deposition of the Co bottom electrode it is slightly oxidized (left). Subsequent deposition of Al will cause the oxygen to move out of the electrode into the Al.

gradients in concentration of O and/or Al throughout the barrier, which are created as a result of the oxidation process. A direct correlation between the asymmetry in the barrier and the magnitude of TMR is reported as well.

In order to increase the TMR by preventing such an asymmetry, some modifications to the simple oxidation process are often applied. Usually this is accomplished by creating a reservoir of oxygen at the interface with the bottom electrode. In a later step, this reservoir is supposed to fill the Al/Al$_2$O$_3$ from the bottom up in order to create a more homogeneous barrier.

The first method in which such a reservoir is used is to first oxidize the surface of the bottom electrode before the deposition of Al, as shown in Fig. 2.4. The subsequent deposition of Al will cause an unstable situation since the Gibbs free energy of CoO is larger\(^8\) than the Gibbs free energy of Al$_2$O$_3$ [Dea92]. Since Al$_2$O$_3$ has a lower energy, the oxygen will move into the aluminum. This is applied by Sun and Freitas \emph{et al.} [Sun99] and Kuiper and Kottler \emph{et al.} [Kui01b]. Tsunekawa \emph{et al.} [Tsu04] used radical beam oxidation and created MTJs with 60\% TMR at room temperature. Before deposition of the aluminum, the surface of the bottom electrode was exposed to oxygen at only $10^{-5}$ Pa. Kottler and co-workers found that, when the Co bottom electrode is partially oxidized, up to 1 nm of Al can be completely oxidized by oxygen from this reservoir. Annealing, \emph{i.e.} bringing the sample in a non-reactive atmosphere (\emph{e.g.} high vacuum, or argon) to a high temperature, can enhance this homogenizing process even further as shown by Koller \emph{et al.} [Kol04b]. This technique is suggested to be less sensitive to over-oxidation because the Al$_2$O$_3$ at the bottom acts as a diffusion barrier to oxidation from the top.

The second method involves a small amount of intentional over-oxidation. A gradient of Al and/or O now exists in the barrier layer. After the top electrode and capping layers are deposited, the junction is subjected to an annealing step, which causes the oxygen to leave the bottom electrode into the Al.

\footnotesize\textsuperscript{8}The same holds for the other ferromagnetic materials often used in MTJs.
and move into the barrier, thus resulting in a more homogeneous barrier layer. This procedure was performed by, for instance, Song et al. [Son00], Dimopoulos et al. [Dim01b], and Roos et al. [Roo02]. In all cases, the barrier is homogenized and the TMR is increased.

Several groups attempted to create more homogeneous barriers without oxidation of the bottom electrode by applying a two-step process, each step being comprised of Al deposition and oxidation. Yoon et al. [Yoo01] applied this technique with plasma oxidation, Das et al. [Das03] with natural oxidation (see also section 2.2.2) and Zhang et al. [Zha03] with a slow ion beam process. For all methods, it is reported that the TMR increases slightly in junctions with a two-step process with respect to a one-step process. The $R \times A$ product increases, often by as much as one order of magnitude (see for example [Zha03]).

In a comparison between single-step and two-step oxidation experiments using XPS, Yoon found that indeed the concentration of O in the barrier is more homogeneous than results from single-step plasma oxidation [Yoo01]. The TMR of the two-step oxidized junctions was indeed higher, although not by much.

### 2.3.3 Pinholes in the barrier

A pinhole is a path of relatively high conduction between the two electrodes, through the barrier layer [Oli04]. Often this is a metallic short due to inhomogeneous oxidation, or a thin part of the barrier due to inhomogeneous deposition of the aluminum prior to the oxidation, or possibly an impurity in the oxide that allows for faster tunneling in two steps. Pinholes in the barrier lower the specific resistance of a tunneling barrier. Additionally, pinholes can decrease the TMR in several ways. First, by creating a strong direct magnetic coupling between the two electrodes, shown in Fig. 2.5a, the free layer no longer switches independently from the bottom electrode.

![Figure 2.5: The effect of pinholes: a metallic connection between the electrodes concentrates a non-spin-polarized current (a). A direct connection between the magnetic layers causes a coupling between the electrodes, inhibiting individual switching of the layers.](image-url)
2.4. Conclusions

This makes a fully anti-parallel alignment impossible resulting in a decreased TMR \cite{Wan03, Zha03}. The observation of a sharp increase in coupling between the two layers, for example by MR measurements, as the barrier thickness is decreased, is often considered as the onset of pinhole formation. The second negative aspect of pinholes is that the largest part of the current through the junction will run via a normal metallic contact instead of proper spin-dependent tunneling, as in Fig. 2.5b.

Zhang et al. \cite{Zha03} found in junctions with a deposited Al thickness of 0.65 nm indications for pinholes. He states that these pinholes are created due to local variations in deposited Al thickness.

Han et al. report on junctions in which the aluminum (0.9 nm) was underoxidized \cite{Han04b}. The as-deposited junctions showed a low resistance (820 \( \Omega \cdot \mu \text{m}^2 \)) and practically no TMR (0.5%). However, after an annealing step, both the junction resistance and the TMR increased enormously to 30 k\( \Omega \cdot \mu \text{m}^2 \) and 43\%, respectively. In TEM measurements on samples that were not annealed, pinholes with a diameter of a few nm are visible. It is not reported whether pinhole-like features were still visible after annealing.

Moon \cite{Moo02} shows that in otherwise identical conditions, the usage of a two-step oxidation process instead of a single-step process increases the TMR as well as the R\( \times \)A product by a factor of two to three. Together with the observation that the magnetic coupling between the bottom and top electrode is lower in junctions fabricated by the two-step process, he concludes that the two-step process creates tunnel barriers with a much lower pinhole density.

2.4 Conclusions

From this review on recent experiments towards better tunnel barriers, it may be clear that enormous efforts have been done to enhance junction properties since the first demonstration of high TMR by Moodera and coworkers. With various techniques it has been tried to improve the properties of the insulating barrier layer, such as thermal oxidation, UV oxidation, and oxidation using radicals or ions. Currently, junctions made by thermal oxidation already match the increasing demands for application in high-density and high-speed MRAM stated in section 1.3. For actual implementation in production processes, however, thermal oxidation is often considered to be a slow step, resulting in a low throughput. Plasma oxidation is much faster, and results in generally high values of TMR, although the R\( \times \)A products are still too high for the signal-to-noise-ratio that is aimed at in MRAM.

Modifications to the standard oxidation procedures proposed for decreasing the R\( \times \)A product of plasma-oxidized junctions, like two-step oxidation and pre-oxidation of the bottom electrode, have not yet resulted in junctions
that match the MRAM demands. As has already been stated in the intro-
duction, before the low processing time and high TMR of plasma oxidation
can be combined with the low $R \times A$ product of thermally oxidized junctions,
more knowledge of the plasma oxidation process is necessary.
Chapter 3

A Theoretical Approach to Oxidation Processes

3.1 Introduction

The growth of oxide layers on metals, together with similar processes such as the formation of sulfide and iodide layers on metals, has been studied since the beginning of the 20th century. There is one characteristic that distinguishes these processes from other chemical processes: after the formation of the first (top) monolayer of oxide, the two reactants are separated from each other by their reaction product, the oxide. Furthermore, the separation becomes greater as the process proceeds. This means that an extra step is needed for the reaction to continue, namely the transport of one or both of the two reactants towards the other, as shown in Fig. 3.1. Generally, it is the transport of (one of) the reactants that is limiting the reaction rate of the oxidation process.

Figure 3.1: Schematic overview of the reaction steps of an oxidation process after the first monolayer has been formed. In the left figure, it is the oxygen O that diffuses into the oxide towards the metal-oxide interface in order to form a new molecule of oxide MO. In the right figure, metal atoms (M) diffuse through the oxide, towards the oxide surface.
Chapter 3. A Theoretical Approach to Oxidation Processes

After the first empirical growth law, connecting film thickness and oxidation time, had been established, theoretical models that explained the observed behavior have been sought for. This is much more complicated than simply considering diffusion of oxygen into the metal as will become clear in the following sections.

In this chapter, we focus on the comprehension of the process itself. First, various existing models that explain the thermal oxidation of metals are introduced. Later, we introduce adaptations to these models in order to incorporate plasma oxidation as well as the influence of the layer structure of a typical tunnel junction. These adaptations will be compared with measurements in chapters 6 and 7.

3.2 Models for thermal oxidation

3.2.1 Introduction

Modelling of reaction processes deals with the determination of rate laws and growth (or time) laws. A rate law connects the reaction rate $v$ to certain process parameters, for example the temperature $T$, the pressure $p_{O_2}$ of the oxygen and the thickness $l$ of the already formed oxide:

$$v = \frac{dl}{dt} = v(p_{O_2}, T, l, \ldots). \quad (3.1)$$

A growth law is the integration of a rate law over the reaction time $t$, giving the oxide thickness as a function of time and the process parameters:

$$l = \int_0^t v dt = l(p_{O_2}, \ldots, t). \quad (3.2)$$

The structure of the resulting oxide layer can affect the rate of oxidation as well, and furthermore, the oxidation conditions may have an influence on the resulting structure of the oxide. The latter effect has been observed in, for example, the oxidation of vanadium at various pressures [Fro91]. This is neglected for the moment.

It will be assumed for the discussion in this chapter that already some small amount of oxide is formed. As mentioned above, the process is composed of several individual reaction steps. In Fig. 3.1a, the most simple view of an oxidation process after some oxide has been formed is shown. The picture contains the necessary steps to form more oxide: gas molecules arrive at the surface, are physisorbed and chemisorbed, diffuse through the initial oxide, and react with metal atoms (or ions). For the oxidation of e.g. silicon and copper it is found that this picture is correct. However, it is not necessary that oxygen is the diffusing species; in the case of metals consisting of small atoms it is found that those metal atoms diffuse through the
oxide towards the surface where they can react with oxygen. In the latter case, the new oxide is created on the solid-gas interface (Fig. 3.1b), in the former case the oxide grows at the metal-oxide interface.

Generally, one of the steps mentioned above is a bottleneck, limiting and therefore determining the rate of the oxidation. However, in real systems, two or more steps may be rate limiting in different stages of the oxidation process, which implies that a thorough investigation of each step is necessary before the problem can be solved at each stage. In the next section, several models concerning various stages and circumstances will be discussed.

### 3.2.2 Models proposed in literature

Most metals will very rapidly form an initial oxide; the reaction coefficient $S$ is practically unity if the metal is pure or covered with only 1 or 2 ML of oxide. Vanadium and titanium have a constant reaction probability of 1 up to even 4 ML of absorbed oxygen, Ag and Cu only have unity reaction probability if the surface is completely uncovered, see [Fro78]. If the reaction coefficient $S$ is constant (as a function of thickness), a fraction $S$ of the oxygen that arrives at a bare metal surface will be consumed. The rate is therefore limited by the supply of oxygen, given by

$$F = \frac{p}{\sqrt{2\pi mk_B T}}$$

in molecules per m$^2$ per second, where $p$ is the pressure (in Pa) and $m$ is the mass of an oxygen molecule (kg). This means that the rate depends on the pressure:

$$\frac{dl}{dt} = \frac{2\Omega_{\text{ox}}^O S p}{\sqrt{2\pi mk_B T}} \quad \Rightarrow \quad l(t) = \frac{2\Omega_{\text{ox}}^O S pt}{\sqrt{2\pi mk_B T}},$$

where $l$ is the oxide thickness (m) and $t$ is the time (s). The constant $\Omega_{\text{ox}}^O = 1.4 \cdot 10^{-20}$ m$^3$ is the volume of aluminum oxide formed per O-atom, converting the number of O-atoms per m$^2$ to the oxide thickness$^1$. The factor two accounts for two oxygen atoms per oxygen molecule that arrives at the surface. This is the linear growth law, valid for oxide thicknesses up to 1 or 2 ML.

In the case of aluminum, the reaction coefficient is determined for perfect Al(111) crystal surfaces [Ost97], of which it has been reported that oxygen has a rather low sticking probability, about $5 \cdot 10^{-3}$ if the gas molecules are at room temperature. In most experiments performed in this thesis the pressure is of the order of 10 Pa, such that the first monolayer of oxide on a bare metal surface will be formed within approximately 10 ms.

$^1$Al$_2$O$_3$ contains $7.1 \cdot 10^{28}$ O-atoms per m$^3$, hence $\Omega_{\text{ox}}^O = 1.4 \cdot 10^{-29}$ m$^3$. 

The reaction probability is reported to rise to unity if the energy of the oxygen molecules is increased to the range of 0.6 to 2 eV [Ost97]. Vibrational excitation of the O$_2$ molecule will also enhance the sticking. The sticking coefficient of Al(111) decreases as the surface coverage increases. Note that these values were derived from experiments on Al(111) crystals and that the sticking behavior is likely to be different for poly-crystalline or amorphous surfaces.

It is acknowledged that the formation of this initial oxide monolayer is extremely complicated and forms a research area on its own, see for example the work of Arranz et al. [Arr96] and Jeurgens et al. [Jeu02b, Jeu02a], but for all oxidation experiments in this thesis the initial oxide layer will be formed practically instantly. We will focus on the continuation of the oxidation process after this initial oxide has been formed. Transportation through the oxide has to take place, generally via diffusion. In an early model for oxidation, developed by G. Tammann [Tam20] and Pilling and Bedworth [Pil23], diffusion of neutral atoms is assumed to be the slowest step, and therefore determining the rate of oxidation. Standard diffusion gives a flux $j_D$ (atoms per m$^2$ per sec.) of aluminum atoms from the metal to the oxide surface:

$$j_D = -D \frac{dC}{dx}, \quad (3.5)$$

where $D$ is the diffusion coefficient (in m$^2$s$^{-1}$), $C$ is the concentration of metal atoms in the oxide (m$^{-3}$) and $x$ is the position in the sample ($x = 0$ is the oxide-gas interface). In quasi-equilibrium, the flux is independent of the position $x$ in the oxide, giving

$$j_D = D \frac{[C(l) - C(0)]}{l}, \quad (3.6)$$

where $x = l$ corresponds to the metal-oxide interface. The rate of growth is now

$$\frac{dl}{dt} = \Omega_{ox}^{Al} j = k l, \quad (3.7)$$

where $\Omega_{ox}^{Al} = 2.12 \cdot 10^{-29}$ m$^3$ is the volume of oxide per Al atom, converting the number of oxygen molecules to oxide thickness, and

$$k = \Omega_{ox}^{Al} D [C(0) - C(l)]. \quad (3.8)$$

Integrating Eq. 3.7, we find the relation between oxide thickness and time that is historically called the parabolic growth law:

$$l^2 - l_0^2 = 2kt, \quad (3.9)$$
where \( l_0 \) is a constant that can account for some initial oxide at the start of an experiment. The model is valid only at high temperatures since diffusion of atoms is a thermally activated process that is negligible at room temperature. In the theory of Wagner [Wag33, Wag36], oxidation by diffusion of charged defects (interstitial ions) at high temperatures (i.e. over 1000 °C) is incorporated. Wagner pointed out that charge neutrality is significant in the oxidation process: at any time and stage, the total charge transported through the oxide, under steady state conditions, must be zero. This concept is known as ambipolar diffusion or the coupled-currents-approach [Fro98]. Since Wagner’s model also depends on diffusion, again a parabolic growth law is found.

Both mechanisms mentioned above cannot explain the very fast initial oxidation at room temperature that is always observed. Mott and Cabrera were the first to point out that the low ion mobility at low temperatures can be greatly enhanced by an electric field over the oxide [Mot39, Mot40]. This field can be set up by electron transfer from the metal to the surface. For the case of very thin layers, where electron tunneling prevails, the logarithmic law was derived by Mott. A special case, where the solution of metal ions into the oxide is the limiting step [Cab49b, Cab49a] leads to an inverse logarithmic law. Inspired by the results in the following chapters and by the article of Cabrera in 1949 [Cab49a], the models that yield the logarithmic growth law and inverse logarithmic growth law will be explained in more detail.

### 3.2.3 The logarithmic growth law

It is assumed that, due to its smaller size, aluminum ions diffuse much faster than oxygen ions in \( \text{Al}_2\text{O}_3 \). Kuiper and coworkers [Kui01a] used an isotope technique in which an Al layer is shortly oxidized with \( \text{O}^{16} \) before continuing with \( \text{O}^{18} \) to confirm that it is indeed aluminum which is the moving species during the oxidation process. Opposite to this, in the case of copper oxidation it was found that vacant lattice Cu-sites migrate inwards towards the Cu / \( \text{CuO}_x \) interface [Mot39], and in silicon oxidation it is found that Si is the mobile species.

For the oxide layer to grow, both ions and electrons must diffuse through the oxide layer, otherwise a charge keeps building up. Electron transport can take place via various mechanisms, see Fig. 3.2a. Direct quantum mechanical tunneling (I in Fig. 3.2a) is the most simple process by which electrons move from the metal to the surface. A second option is thermionic emission into the conduction band of the oxide (II), which requires an activation energy \( \Phi \). Subsequent diffusion (or even ballistic transport) towards the oxide surface

\[^2\text{0.146 nm for O vs. 0.045 nm for aluminium [Wea75]}\]
can occur practically freely. Electron movement via positive holes (III), from the oxide-gas interface inwards, is the third option. An electron is transferred from a filled level of the oxide to a surface level of an absorbed oxygen atom, requiring an activation energy $\Psi$. Now, the positive hole that is left in the oxide can move towards the metal, where it is filled by an electron. In $\text{Al}_2\text{O}_3$ layers thinner than 5 nm, tunneling will prevail above the thermionic emission process [Mot40].

Ions move through the oxide as interstitials via a hopping process, as shown in Fig. 3.2b, assisted by the electrical field set up by electrons at the surface. In the figure, $W$ is the energy barrier for the first hop of an Al-ion from the metal into the oxide.

The growth rate of the oxide depends on the flux $j$ of metal ions crossing the oxide per unit area per unit time:

$$\frac{dl}{dt} = j\Omega_{\text{ox}}^\text{Al},$$

(3.10)

where $\Omega_{\text{ox}}^\text{Al}$ is the volume of the oxide per metal atom (see Eq. 3.7). The flux $j$ is determined by the electric-field-assisted diffusion of ions and electrons through the oxide:

$$j = -D_i \frac{\delta n_i}{\delta t} + E n_i \mu_i$$

(3.11)

$$= -D_e \frac{\delta n_e}{\delta t} - E n_e \mu_e,$$

(3.12)

where $n_i$ and $n_e$ denote concentrations of ions and electrons, $D_i, D_e$ and $\mu_i, \mu_e$ denote ion and electron diffusion constants and mobilities, respectively. $E$ is the electric field in the oxide:

$$\frac{dE}{dx} = \frac{1}{\epsilon_0} (n_i - n_e) e$$

(3.13)
3.2. Models for thermal oxidation

For films that are $< 1$ cm thick, the case which is under investigation here, Mott and Cabrera have shown that space charges in the oxide do not influence the field in the oxide [Mot47]. Two cases can be distinguished:

**A.** The case where $W > \Phi$, which means that it is easier for electrons (Fig. 3.2a) than for ions to enter the oxide (Fig. 3.2b). Therefore, the rate of growth is determined by the diffusion of ions. If $n(x)$ is the number of ions per unit volume at a distance $x$ from the metal-oxide interface, the flow of ions will be

$$ j = D_i \frac{\delta n}{\delta x} . $$

(3.14)

In the oxide, at the metal-oxide interface, the number of Al ions $n_0$ is given by

$$ n_0 = N e^{-W/k_B T} , $$

(3.15)

where $N$ is the number of interstitial positions per unit volume ($\approx 10^{22}$ m$^{-3}$).

Using $\delta n/\delta x = n_0/l$, where $l$ is the oxide thickness, we obtain

$$ j = n_0 D_i / l , $$

(3.16)

which gives, combined with Eq. 3.10,

$$ \frac{dl}{dt} = \frac{n_0 \Omega^\text{Al}_\text{ox} D_i}{l} , $$

(3.17)

or

$$ l^2 - l_0^2 = 2 n_0 \Omega^\text{Al}_\text{ox} D_i t . $$

(3.18)

This is a parabolic law of growth, valid for small thicknesses.

**B.** The case where $\Phi > W$. This means that ions can enter the oxide more easily than electrons. For very thin films, roughly below 4 nm (see [Mot47]), electrons pass through the oxide via quantum mechanical tunneling (see section 1.2.1) and form negatively charged atoms and molecules at the surface. The rate is then determined by the tunneling effect. Since the tunnel current depends exponentially on the thickness of the oxide,

$$ j_{\text{tun}} = c e^{-l/l_0} , $$

(3.19)

where $c$ and $l_0$ are constants, this gives

$$ \frac{dl}{dt} = c \Omega^\text{Al}_\text{ox} e^{-l/l_0} $$

(3.20)

and therefore

$$ l = l_0 \ln \left( \frac{\Omega^\text{Al}_\text{ox} t}{l_0} + c \right) . $$

(3.21)

This is the logarithmic growth law, which is valid for layers thinner than roughly 4 nm.
Chapter 3. A Theoretical Approach to Oxidation Processes

3.2.4 The inverse logarithmic growth law

For the specific case of aluminum oxidation, Cabrera [Cab49a] argued that another mechanism determines the rate of oxidation, leading to another growth law. For very thin oxide layers, electrons tunnel rapidly towards the surface and back, creating an equilibrium between the levels of electrons at the Al/Al₂O₃-interface and oxygen surface atoms. Shown in Fig. 3.3a is the initial state, and in Fig. 3.3b the electron equilibrium is established. The potential $V$ over the oxide is then equal to the initial difference between the Fermi level and the oxygen levels, and is therefore not dependent on the thickness of the oxide layer as long as the thickness is not too large. The electric field in the oxide, $E = V/l$, can be very high so that each metal ion that goes into solution (in Fig. 3.2: the first “hop”) in the oxide will diffuse rapidly towards the surface. The chance per unit time that an ion hops over the barrier $W$ (without field) is $\nu \exp(-W/k_B T)$. In the presence of the field

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.4}
\caption{Energy diagram of metal ions in the oxide with a field present. The dotted line represents the case without field, see Fig. 3.2. The field $E$ lowers the barrier $W$. The distance from point P to the top of the barrier is represented by $a$.}
\end{figure}
3.2. Models for thermal oxidation

with strength $E$ (see Fig. 3.4) the barrier height is modified:

$$\nu \exp \left( - \frac{(W - qaE)}{k_B T} \right), \quad (3.22)$$

where $\nu$ is the attempt frequency of ion hopping ($\approx 10^{12} \text{ s}^{-1}$), $a$ is the distance as denoted in the figure and $q$ is the charge of the ion. The growth rate of the oxide is then

$$\frac{dl}{dt} = N \Omega_{\text{Al}}^{\text{ox}} \nu \exp \left( - \frac{W}{k_B T} \right) \exp \left( \frac{qaE}{k_B T} \right), \quad (3.23)$$

where $N$ is the number of potentially mobile metal interface atoms per unit area. This number is smaller than the total number of Al atoms at the interface\(^3\); possibly only atoms that are less tight bound, for example those located at or near surface defects, will be available. Cabrera et al. estimated $N$ to be $\approx 10^{19} \text{ m}^{-2}$ [Cab49b]. Equation 3.23 is conveniently written as

$$\frac{dl}{dt} = u \ln(l/\ell_1), \quad (3.24)$$

with $l_1 = qaV/k_BT$, and

$$u = u_0 \exp(-W/k_BT), \quad (3.25)$$

and $u_0 = N \Omega_{\text{Al}}^{\text{ox}} \nu$. The growth rate is very large for small oxide thicknesses. For a constant voltage $V$, the growth has a limiting thickness at low temperatures. The temperature range for which there is such a limit can be determined. Take the limiting thickness $l_L$ as the thickness at which the rate has dropped to for example one layer per $10^5$ seconds (arbitrarily chosen, but is not very critical), this yields, with $u_0 \approx 100 \text{ m/s}$, $\exp(l_L/l_1 - W/k_BT) = 10^{-17}$. Substituting for $l_1$, we obtain for the limiting thickness

$$l_L = \frac{Vaq}{W - 39k_BT}. \quad (3.26)$$

This defines a critical temperature $W/39k_B$ below which the oxide has a limiting thickness and above which the oxide continues to grow. For aluminum, Cabrera extracted $W = 1.8 \text{ eV}$ and $a = 0.35 \text{ nm}$ from experiments. The critical temperature for aluminum is thus 530 K and the limiting thickness at room temperature was measured to be 2.0 nm, giving a voltage $V$ of approximately 2 V. The experimental value for the critical temperature was found by Cabrera to be approximately 570 K, in reasonable agreement with the theory.

\(^3\)Al atoms are approximately 0.15 nm in diameter, resulting in about $10^{19}$ Al atoms per m\(^2\).
At room temperature, \( l_1 \) is approximately 15 nm; for Eq. 3.24 to be valid the oxide must be thinner than this value. This condition is met for all experiments in this thesis. From the rate equation (Eq. 3.24) the following approximated growth law was derived by Cabrera and Mott:

\[
\frac{l_L}{l} = \ln(t) - \ln\left(\frac{l_2^L}{l_1 u}\right),
\]

(3.27)

which is the well-known inverse logarithmic law. Additional to being a rather crude approximation and not an actual solution of the rate equation (deviations with respect to numerical calculations of 10 to 56\% can occur, see [Ghe73]), this law is inconvenient since it relies on \( l_L \), which depends on the arbitrary definition of “zero growth” given in Eq. 3.26. Furthermore, it is not possible to plot experimental data according to this law in order to distinguish it from the logarithmic law. A better approximation was deduced by Ghez [Ghe73]:

\[
\frac{l_1}{l} = -\ln\left(\frac{t + \tau}{l^2}\right) - \ln(l_1 u),
\]

(3.28)

for which experimental data are more easily plotted as \( 1/l \) versus \( \ln(t/l^2) \), if \( \tau \) (a constant) is smaller than the smallest measured time. This should yield a straight line from which the parameters \( l_1 \) and \( u \) can be deduced.

In the case of the oxidation of tantalum, the formula of Ghez appears to describe the measurements by Vermilyea very well [Ghe73]. Furthermore, a correct temperature dependence in \( u = u_0 \exp\left(-\frac{W}{k_B T}\right) \) (Eq. 3.24) was found. Only for the pre-factor \( u_0 = N\Omega_{ox}^{Al} \nu \) the experimentally determined value was 4 orders of magnitude lower than was estimated. This was explained by assuming that only 1 in \( 10^4 \) atoms can participate in the transport, possibly because these atoms are located at a defect at the metal/metal-oxide interface.

### 3.2.5 Short summary

Summarizing, we described two models that are often quoted in literature and are likely to be valid for the thermal oxidation of aluminum at low temperatures (below 600°C). Both models describe the continued growth of the oxide after an initial oxide (1 or 2 ML, 0.25 - 0.5 nm) has been formed. The models are valid for thin oxide layers, below 4 nm.

In the first model, discussed in section 3.2.3, the rate is determined by the field in the oxide that is set up by tunneling electrons, leading to the logarithmic law:

\[
l = l_0 \ln\left(\frac{\Omega_{ox}^O t}{l_0} + c\right).
\]

(3.29)
The second model, which was discussed in section 3.2.4, has as the rate-determining step the solution of positive Al-ions in the oxide (i.e. the first “hop” in Fig. 3.2, with an activation barrier $W$), which is dependent on the field in the oxide. This leads to the growth law of Ghez (Eq. 3.28), to which we will refer as the inverse logarithmic growth law:

$$\frac{l}{l_1} = -\ln\left(\frac{t + \tau}{l_2^2}\right) - \ln(l_1 u).$$

The logarithmic growth law and the inverse logarithmic growth law are shown in Fig. 3.5, together with the parabolic growth law which results from a simple diffusion model, which was mentioned in section 3.2.2:

$$l^2 - l_0^2 = 2kt.$$

It can be easily observed that the inverse logarithmic growth displays a characteristically higher initial growth rate than the logarithmic growth. More accurate solutions are usually obtained by numerical methods, see for example the work of Fehlner [Feh86] and Fromm [Fro98]. In this thesis the focus will be on the two analytical models, enabling us to illustrate the influence of the layer structure and a plasma more clearly.

![Figure 3.5: Comparison between sample curves of the growth laws from the various models that were discussed.](image)

### 3.2.6 Influence of the thickness of the aluminum

The models discussed so far apply to a thick (semi-infinite) layer of aluminum whereas in magnetic tunnel junctions the aluminum thickness is typically between 0.6 and 2.5 nm (3 to 10 monolayers). In this section we examine the possible influence of the presence of the Co-Al interface on the two material parameters that play an important role in the oxidation models:
the energy of solution \( W \) and the work function (with respect to the oxide) \( \Phi \).

The presence of non-Al atoms, cobalt in this case, will cause some Al atoms to have a bonding energy that is different from the Al-Al bonding in bulk aluminum, see Fig. 3.6. Co-bonded Al-atoms will thus have a \( W \) that is different from Al-bonded Al-atoms, and according to Eq. 3.23, the oxidation rate \( \frac{dl}{dt} \) will be modified. Whether a Co-Al bond is stronger or weaker than an Al-Al bond depends strongly on the exact structure, see [Wid98]. This effect is thought to have a small “range” of only one monolayer (i.e. approximately 0.25 nm) and is therefore not considered to be significant until the oxidation of the aluminum is practically complete.

![Figure 3.6: The Co-Al interface: the atoms in layer 1 will have different bonding energies compared to atoms in layers 2 and 3. Layer 2 can already be considered to be practically “bulk”.

The work function \( \Phi \), in Fig. 3.2, controls the field across the oxide. If \( \Phi \) is increased (i.e. the energy level of the electrons in the aluminum is lowered), the equilibrium field and potential difference in the oxide will be lower and hence the rate of oxidation will be smaller according to Eq. 3.23. The work function can be modified in several possible ways. First, cobalt has a higher work function than aluminum\(^4\), which causes a contact potential of 0.8 V to be set up. In a thin region around the interface, electrons from the aluminum will move into the cobalt, similar to the depletion region in a semiconductor pn-junction. The depletion region is of the order of the Thomas-Fermi screening length [Kit96]

\[
R_{TF} = 0.5 \left( \frac{n}{a_0^3} \right)^{-1/6},
\]

where \( n \) is the electron density at the Fermi level and \( a_0 \) is the Bohr radius. In the case of aluminum, \( n = 1.8 \cdot 10^{29} \) m\(^{-3} \) [Kit96], the screening length is approximately 0.05 nm. This implies that outside this region, much less than one atomic distance away from the Co-Al interface (0.25 nm), no influence of the lower work function of cobalt is to be expected.

\(^4\)Al: 3.38 eV, Co: 4.21 eV, from [Kle38]. Reported values vary (see [Wea75, p.E81-82]), therefore two values of the same reference were taken to ensure mutual comparability. Note that \( \Phi \) can also depend on the crystal plane.
3.2. Models for thermal oxidation

Secondly, removing an electron from the metal surface and bringing it some distance away, as in Fig. 3.7, causes the mobile electrons at the metal surface to rearrange themselves in order to expel the field from the metal. This surface charge does not extend very far into the metal, of the order of the Thomas-Fermi screening distance mentioned above. Changes in this effect due to the presence of a different metal will therefore not play a significant role in the oxidation process until the oxidation front has practically reached the Co-Al interface.

So far, the influence of another conducting substrate material (cobalt) has been discussed, leading in all cases to effects that only affect the oxidation of the last Al monolayer directly attached to the metallic substrate. In the case of an insulating layer under the aluminum, another effect will appear, namely the decreasing number of electrons that is available for tunneling to the surface. A similar effect will be discussed in the next section.

3.2.7 Influence of the layer morphology

In all models discussed above it is assumed that both the aluminum layer and the resulting oxide are homogeneous. It has been observed, however, that sputter deposition of aluminum on a cobalt underlayer results in a layer that consists of grains of 3 to 20 nanometers in diameter, depending on deposition parameters. See, for example the work of Ando et al. [And02] and Kurnosikov et al. [Kur01]. After oxidation, the oxide has a similar grain-like structure, of which an example is shown in Fig. 3.8.

The grains and the grain-boundaries have a different atomic structure resulting in different diffusion coefficients [Atk85] and different values of the conduction band energy of the oxide. It is generally assumed that oxidation of the boundary is much faster than the grain, therefore possibly resulting in two different time scales in the oxidation process. In addition, it is argued that the initial oxidation of the grain-boundaries helps the oxidation of the grain interiors by side-ways diffusion [Kui01a]. In view of sections 3.2.3 and 3.2.4, however, this seems unlikely since no electrical field can be built up.
over the boundary-oxide in order to stimulate sideways diffusion.

The grain structure can lead to a deviation of bulk oxidation as well. In natural oxidation of a homogeneous layer, electrons coming from the metal tunnel through the oxide towards the surface, where they set up the driving field for the oxidation process. A redistribution of charges in the metal is induced in the metallic plane in order to expel the field caused by an electron at the surface. Consider now a spherical metallic grain in a non-conducting matrix (i.e. Al$_2$O$_3$) of which an electron is being moved to the oxide surface. The charge distribution in the sphere induced by an electron at the oxide surface is completely different from the distribution in a flat layer. This effect is described and quantified by Wood [Woo81] using the image charge method. Additionally, if the sphere is assumed to be isolated, the removal of one electron will leave the sphere charged, increasing the work function. Combining these two effects, Wood finds that the work function increases as the radius decreases:

$$
\Phi(eV) = \Phi_\infty + \Delta \Phi, \quad \Delta \Phi = \frac{3}{8} \frac{e^2}{\epsilon_0 \epsilon_r R} = \frac{0.54}{\epsilon_r R(\text{nm})},
$$

where $R$ is the radius of the metallic sphere and $\Phi_\infty$ is the work function for the planar metal. In order to correct for the vacuum conditions used in Woods’ model, an extra factor of $\epsilon_r$, the relative permittivity of the Al$_2$O$_3$, was added. $\epsilon_r$ is assumed to be approximately 10, see [Res02]. When $R = \infty$, corresponding to a flat layer, the extra term vanishes. For grains of 1 nm in diameter the work function is increased by 0.1 eV, which is significant since the work function $\Phi$ appears in the exponential in Eq. 3.23.

Effectively, the issue mentioned above modifies the electron equilibrium between the metal and the O-levels at the surface resulting in a lower field in the oxide and therefore a lower rate of oxidation as well. This means that during the oxidation process the work function of the aluminum might

---

**Figure 3.8:** A 0.9 nm film is oxidized and measured by STM (20 nm × 20 nm). A grain-like structure is observed. Picture taken from [Kur01].
change as the size of the metallic grain is decreased due to oxidation, as shown in Fig. 3.9a. Additionally, it has been reported that the initial grain size, before oxidation starts, can depend on the deposited layer thickness [Tu03], as shown in Fig. 3.9b. In conclusion, we expect that the oxidation process is influenced by the layer morphology, which initially depends on the deposited layers and changes as the oxidation proceeds.

Figure 3.9: a) During oxidation the size of the metallic center of a grain decreases. b) Depositing a thicker layer can induce the growth of larger grains.

3.3 Plasma characteristics

3.3.1 Introduction

The two most obvious features of a plasma are the fact that it emits light and the presence of charged particles. These particles are in the first place electrons, coming from ionized atoms, and several types of ions: both positive and negative, both charged atoms and molecules. Besides the charged particles also an extended variety of neutrals exist: atoms and molecules in their ground states and in excited states, and radicals: atoms or molecules with one or more unbounded electrons. All these particles play different roles in reactions, and because the reaction speed can depend on the density and kinetic or internal energy of the reacting particles, it is essential to study the composition and energy distributions of a plasma. The following sections describe several typical characteristics of plasma’s, reactions in plasmas and at surfaces, and, most importantly, the way the plasma can influence the oxidation dynamics.

3.3.2 Plasma characteristics and sheaths

A plasma is a (partially) ionized gas. Although charged species exist, a plasma is macroscopically neutral. In a DC glow discharge, as is used in this research, electrons and ions gain energy by acceleration in an applied field, and in collisions some energy is transferred to the background gas. Due to their small mass, energy transfer from electrons to oxygen molecules is not
efficient, hence electrons will have a higher temperature ($T_e$, in eV) than the heavier particles. Typically, the electron temperature in a glow discharge ranges from 1 to 5 eV. The ion temperature ($T_+$) in glow discharges is always lower than the electron temperature, usually close to the temperature of the background gas due to more efficient energy and momentum transfer [Lie94].

Two characteristic length scales that are important for many processes in plasmas will be introduced here. The *mean free path*, $\lambda_{\text{mfp}}$, is the average distance a particle can travel without a collision. For the plasmas currently under investigation, this distance is of the order of a few millimeters for collisions of electrons with O$_2$ and a millimeter for O with O$_2$ [Lie94, page 18]. The *Debye length* [Lie94]

$$\lambda_D = \sqrt{\frac{\epsilon_0 k_B T_e}{e^2 n_e}} = \sqrt{\frac{\epsilon_0 T_e}{en_e}}$$

(3.34)

is a screening distance, over which charge can be separated. For example, if an extra fixed charge is introduced in a plasma, its presence will be “felt” in a sphere with a radius of the order $\lambda_D$ around the charge. The particles in this sphere are rearranged, such that outside the sphere the field caused by the inserted charge is screened and the plasma is neutral again.

Above any surface (for example the sample that must be oxidized) inserted in a plasma a special phenomenon occurs: due to the high thermal velocity of electrons with respect to ions, electrons will charge the surface negatively, as in Fig. 3.10.

This negative surface charge will enable only those electrons with high energy to reach the surface. In addition, positive ions will be accelerated towards the surface. In equilibrium, there will be a non-neutral region called a plasma sheath that has a higher density of positive ions than electrons. Assuming that no collisions take place in the sheath when the pressure is

![Figure 3.10: A plasma sheath above the sample surface. Fast electrons charge the surface. More electrons will be repelled, ions are attracted. A positively charged region develops above the negative surface, creating a potential difference between the sample and the plasma.](image)
low, the thickness $s$ of the sheath, expressed in Debye-lengths ($\lambda_D$), is:

\[ s = \lambda_D \left( \frac{2V_0}{T_e} \right)^{1/2}, \quad (3.35) \]

where $V_0$ is the sheath voltage:

\[ V_0 = T_e \ln \left( \frac{M_+}{2\pi m_e} \right)^{1/2} \quad (3.36) \]

Here, $M_+$ and $m_e$ are the positive ion mass and the electron mass, respectively. The sheath potential is therefore a few times the electron temperature; for glow discharges this results in a potential of the order of 5 to 10 eV that accelerates ions towards a surface. The sheath thickness is a few Debye-lengths. In the case of a plasma of an electronegative gas\(^5\) like oxygen, the sheath voltage is lower due to a higher effective mass of the negative particles. This is negligible as long as $n_e/n_- > 1$. It must be noted that only a very basic view of plasma sheaths is given here; for a more extensive discussion on plasma sheaths see Lieberman [Lie94].

### 3.3.3 Plasma reactions

In general, a plasma is a very reactive environment because of the large amount of reactive particles, like several ions ($\text{O}^-, \text{O}_2^-, \text{O}_2^-$, $\text{O}^+$, $\text{O}_2^+$) and neutrals ($\text{O}$, $\text{O}_2$, $\text{O}_3$) either in ground- or excited state, of which the latter is often more “reactive”. These particles are produced and removed by a number of processes [Smi01a], cf. table 3.1 for a selection.

Reaction R1 is the main process in which electrons and ions are created. Direct recombination, $\text{e}^- + \text{O}_2^+ \rightarrow \text{O}_2$, is under low-pressure unlikely to happen in the gas-phase because of conservation of momentum and energy. With a third particle to facilitate conservation of momentum acting as a spectator, this reaction is possible, but 3-particle collisions do not occur frequently in low-pressure plasmas. Therefore, direct recombination will in practice only happen at surfaces as in reaction R2, the electron can be supplied from the surface itself or the ion is adsorbed at the surface waiting for an electron to arrive. Recombination in the gas phase can occur via dissociative recombination; reaction R3. Often, one of the reaction products is in an electronically excited state. R3 to R7 are typical reactions in which reactive radicals and ozone are created. Reaction R4, positive-negative ion recombination, is often the dominant reaction for negative ion loss. Reactions R8 and R9 create and destroy a more complex particle, ozone. The three-body reaction in the gas phase is, under our experimental conditions,\(^\text{a}\)

\(^{\text{a}}\text{In an electronegative plasma, negative ions are formed easily.}\)
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<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$e^- + O_2 \rightarrow O_2^+ + 2 e^-$</td>
<td>ionization</td>
</tr>
<tr>
<td>R2</td>
<td>$e^- + O_2^+ + S \rightarrow O_2 + S$</td>
<td>recomb. at surface</td>
</tr>
<tr>
<td>R3</td>
<td>$e^- + O_2^+ \rightarrow O^* + O$</td>
<td>dissoci. recomb.</td>
</tr>
<tr>
<td>R4</td>
<td>$O^- + O^+ \rightarrow O^* + O$</td>
<td>pos-neg ion recombination</td>
</tr>
<tr>
<td>R5</td>
<td>$e^- + O_2 \rightarrow O^- + O$</td>
<td>electron attachment</td>
</tr>
<tr>
<td>R6</td>
<td>$O_2^- + O_2 \rightarrow O_3 + O + e^-$</td>
<td>neg. ion detachment</td>
</tr>
<tr>
<td>R7</td>
<td>$e^- + O_2 \rightarrow O^* + O + e^-$</td>
<td>dissociation</td>
</tr>
<tr>
<td>R8</td>
<td>$O + O_3 \rightarrow 2 O_2$</td>
<td>chemical reaction</td>
</tr>
<tr>
<td>R9</td>
<td>$O + O_2 + S \rightarrow O_3 + S$</td>
<td>three-body association</td>
</tr>
<tr>
<td>R10</td>
<td>$e + O$ (or $O_2$) $\rightarrow O^* (or O_2^*) + e^-$</td>
<td>direct excitation</td>
</tr>
<tr>
<td>R11</td>
<td>$h\omega + O_2 \rightarrow O_2^+ + e^-$</td>
<td>photo ionization</td>
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<tr>
<td>R12</td>
<td>$h\omega + O_2^- \rightarrow O_2 + e^-$</td>
<td>photo detachment</td>
</tr>
<tr>
<td>R13</td>
<td>$O^<em>$ or $O_2^</em>$ $\rightarrow O + h\omega$</td>
<td>photo emission</td>
</tr>
<tr>
<td>R14</td>
<td>$O^* + S \rightarrow O + S$</td>
<td>quenching</td>
</tr>
</tbody>
</table>

Table 3.1: A selection of possible reactions in a plasma [Smi01a, pag.305]. S denotes a “spectator” for absorbing impusl and energy, which can be an $O_2$ molecule or a surface. Excited species are denoted by a star (*)

unlikely to happen. If the wall is the spectator, and one or both species is already absorbed at the wall, the reaction probability is very high.

Atoms and molecules can become excited by direct collision (reaction R10) or in a dissociation reaction like R7 where the surplus of kinetic energy of the electron is converted to internal energy of one of the reaction products. These excited particles can decay via emission of a photon (R13) or in a quenching collision with another particle or a surface (R14). Photons can play an extra role in a plasma by photo detachment or photo ionization (reactions R11 and R12).

Next, we investigate qualitatively how the various reactions and plasma parameters could influence the oxidation process.

3.4 Influence of a plasma on oxidation dynamics

3.4.1 Introduction

In a plasma, aluminum oxidizes much faster than in pure oxygen gas, as has already been pointed out in chapter 2. By stating that the higher oxidation rate is caused by the “reactive particles” in the plasma it is overlooked that an oxidation reaction is very complex (see previous sections), and therefore the possible influence of a plasma on the oxidation process should be
3.4. Influence of a plasma on oxidation dynamics

carefully considered in more detail. In this section we will describe various possible interactions between the plasma and the aluminum and aluminum oxide surfaces.

3.4.2 Negative charge at the oxide surface

In both models described above, the field in the oxide due to negative charging of the surface is considered crucial for the oxidation reaction. In a natural or thermal oxidation process, these electrons are supplied by the metallic substrate itself, charging adsorbed oxygen atoms negatively. A plasma could act as an extra supply of surface charge in the form of electrons or negative oxygen ions. This negative surface charging occurs in all plasmas in the formation of a plasma sheath, as described in section 3.3.2. Additional negative surface charge could affect the oxidation process by an increase of the field in the oxide, thereby accelerating the field-assisted diffusion of aluminum ions towards the surface. Macroscopically, it is obvious that the field of the extra surface charge is cancelled by the net positive charge of the sheath region. On the scale of nanostructures, however, this must be examined in more detail.

In order to be able to estimate the relevance of the extra charge, the charge density that exists during natural oxidation must be calculated. In a first order approximation, the surface charge \( \sigma_s \) depends on the field across the oxide of thickness \( l \):

\[
E = \frac{\sigma_s}{\epsilon} \quad \rightarrow \quad \sigma_s = \epsilon \frac{V}{l}.
\]

With realistic values (taken from [Cab49a]) \( V = 2 \text{ V}, \ l = 1 \text{ nm}, \) and \( \epsilon = 10\epsilon_0 \), we find during a natural oxidation process a surface charge of \( 10^{17} \) electrons per \( \text{m}^2 \), which, on average, corresponds to one electron on a circular area with a radius of about 1 nm. The additional charge due to electrons from a plasma can be estimated by assuming that the sample is inserted in a typical glow discharge with \( n_e = 10^{16} \text{ m}^{-3} \) and \( T_e = 2 \text{ eV} \). The sheath voltage and thickness are then approximately 10 V and \( 10^{-3} \text{ m} \), with which the charge density at the surface can be calculated approximately similar to Eq. 3.37, resulting in \( \sigma_{\text{plasma}} \approx 10^{115} \) electrons per \( \text{m}^2 \). Being two orders of magnitude lower than the “natural” charge density on the surface, it is expected that the influence of the extra charge is probably not significant for the oxidation process. The actual charge density will be calculated when the electron temperature and density of the plasma that is used are determined, in section 7.4.

The additional supply of electrons at the oxide surface could accelerate the oxidation process in another way, namely by facilitating electron attachment of adsorbed oxygen atoms, resulting in negative oxygen ions that could
move into the oxide layer. Indeed, for the oxidation of silicon it was suggested that this is a possible effect of the plasma, see chapter 2 of [Fra89]. However, if oxygen is not the moving species, which is the case with Al oxidation, this process can be discarded; cf. section 3.2.3.

### 3.4.3 The influence of “reactive particles” at the surface

Ozone and atomic oxygen, potentially present in the plasma under investigation (reactions R3, R4, R6), are often referred to as “reactive particles” which suggests an enhancement of the rate of the oxidation process. The higher reactivity of O and O\textsubscript{3} with respect to molecular oxygen lies in the dissociation step that is often necessary in reactions with O\textsubscript{2}; in the case of O no dissociation is necessary, and in the case of O\textsubscript{3} the dissociation requires a much lower activation energy than the dissociation of O\textsubscript{2}. The supply of O and ozone from the plasma can therefore increase the density of O at the surface.

Both oxygen atoms and ozone have a much higher electron affinity (1.5 eV and 2.1 eV, respectively) than oxygen molecules (0.45 eV [Wea75]), and therefore lower surface levels as compared to O\textsubscript{2}, see Fig. 3.11. In the logarithmic model, this will cause the tunneling current, Eq. 3.20, to increase (see also section 1.2.1) and therefore this will increase the oxidation rate as well. In the inverse logarithmic model, this will cause the electron equilibrium to shift (cf. Fig. 3.2), leading to a higher charge separation, and will thus result in a higher field in the oxide.

It is reported that ozone has a high sticking coefficient as compared to O\textsubscript{2} [Pop02] and atomic oxygen has a sticking coefficient that is even close to unity [Ost97]. If in a natural oxidation process the surface is not fully covered by oxygen, the presence of excited molecules can then provide extra oxygen at the surface, possibly increasing the charge density at the surface. This would result in a higher field in the oxide, and hence a higher rate of oxidation.

![Figure 3.11: Energy levels in the metal, in the oxide and at the surface. Atomic oxygen has lower levels than O\textsubscript{2}.](image)
3.4.4 Excited particles at the surface

In oxygen gas, practically all particles reside in their fundamental ground state. At room temperature, even rotational and vibrational energy in molecules are minimal since the typical energy of the first excited rotational or vibrational state is of the order of 0.2 eV, corresponding to four to ten times $k_B T$. In a plasma, however, collisions with high-energy particles, usually electrons, create a large supply of molecules in excited states, both rotational/vibrational and electronic (reactions R10 in table 3.1). The internal energy “stored” by molecules can range from 0.1 eV to a few eV. Furthermore, in recombination and dissociation reactions reaction products often have a high internal energy (for instance reactions R3, R4, R7). The high internal energy can be released by the particle by emission of a photon. The process in which a particle is de-excited in a collision is quenching:

\[ \text{O}^* + \text{O}_2 \rightarrow \text{O} + \text{O}_2 \quad \text{(Reaction R14 in table 3.1)} \]

The internal energy is converted to kinetic energy, divided over the two reactants. This process can happen at a surface as well, causing energy to be released to the surface. This energy could influence the growth of the oxide in various ways. At first sight, the energy could be transferred to electrons in the aluminum layer, stimulating them to cross the oxide towards the surface. The current induced in this way is called a chemi-current [Ger01] and could increase the field in the oxide, accelerating the oxide growth. However, this process would stimulate the movement of electrons in both directions across the oxide, resulting in no net effect. Secondly, the energy could be transferred to heat in the form of lattice vibrations (phonon excitation), possibly helping the diffusion of ions. This effect of a local increase in temperature will be discussed in section 3.4.7.

As already mentioned in section 3.2.2, vibrationally excited molecules have a higher sticking probability than molecular oxygen in the ground state [Ost97]. As has been discussed in the previous section, a higher sticking probability can increase the charge density at the surface, increasing the electrical field and hence stimulate the oxidation rate.

3.4.5 Ion implantation

Ions with high kinetic energy are able to penetrate a material to some extent. This process, ion implantation, is applied for creating “buried layers” or doped layers in silicon semiconductor technology, see for example [Rub03]. In a plasma, positive oxygen ions can obtain a kinetic energy that is much higher than the thermal energy (room temperature corresponds to 26 meV) by acceleration in plasma sheaths (Fig. 3.10 in section 3.3.2) towards the sample surface; the energy gained in a plasma sheath is typically of the order of 5 to 10 eV. This is much lower than the 1 keV to 3 MeV that is normally
used to implant ions a few tens of nanometers deep [Lie94]. It is not expected that ions with an energy of maximally 10 eV will penetrate the film more than one monolayer\(^6\) [Mul86]). Therefore, oxygen ion implantation as an oxidation process on itself is not considered to be important. Implantation of ions one atomic layer deep is possible, and therefore ion implantation might play a role in the oxidation process as a process that can supply oxygen in the oxide itself, thereby skipping the step of physisorption and subsequent chemisorption. Nevertheless, in both models discussed above this is not a rate determining step.

Roos \textit{et al.} report oxidation measurements using a relatively low energy (30 to 80 eV) ionized atom beam [Roo00b, Roo01]. It is reported that the oxide thickness that can be obtained is finite and that the final thickness is larger at higher ion energies. Simulations using a simple model that includes ion implantation and diffusion roughly display the observed trend. It should be noted that it is easily conceivable that the increase in depth that is observed as the ion energy increases will probably emerge from any simulated process in which the energy (“temperature”) is increased. Hence, further investigations to support this model of ion implantation are needed.

Vernon \textit{et al.} [Ver39] developed a model that resulted in a logarithmic growth law for the oxidation by atom implantation, thereby explaining the observed behavior of the oxidation of zinc at temperatures above 200°C. In the model it is assumed that of a number \(N_0\) of oxygen atoms impinging on the surface, a fraction \(f\) will succeed in penetrating the first oxide layer. Therefore, \(fN_0\) molecules are incident on the second layer, of which again a fraction \(f\) can penetrate to the third layer. If the oxide thickness is \(n\) layers, the number of oxygen molecules reaching the metal-oxide interface will be \(f^nN_0\). Therefore, the rate of oxidation is proportional to

\[
\frac{dl}{dt} = k_1f^nN_0, \tag{3.38}
\]

or, since \(n \propto l\),

\[
\frac{dl}{dt} = k_1f^{k_2l}N_0, \tag{3.39}
\]

where \(k_i\) are constants. Thus

\[
\frac{dl}{f^{k_2l}} = k_3dt. \tag{3.40}
\]

Integrating gives the following oxide thickness:

\[
l = k \log(k't + c). \tag{3.41}
\]

\(^6\)Müller reports that 100 eV ions penetrate a few tenths of nm at maximum.
3.4. Influence of a plasma on oxidation dynamics

However, this oxidation model has a flaw, as pointed out in various reactions on the article by Vernon [Eva39]: what happens with the oxygen molecules that do not penetrate the next layer? Will those molecules stay at those positions, or reflect back? It was reported that if one of these processes is taken into account, no logarithmic behavior can result.

Ion implantation as direct oxidation process is rejected, but a second effect related to accelerated ions, the delivery of energy to the sample, might be of importance. This will be discussed in section 3.4.7.

3.4.6 Plasma radiation

Practically all plasmas emit light, via reaction R13 in table 3.1. Photons with wavelengths ranging from the UV (200 nm, or 5.5 eV) to the infrared (900 nm, or longer) are emitted and can reach the sample surface. Incident radiation can be absorbed and converted to heat or cause an event like photo-emission of an electron.

Thermal heating of the surface layers by radiation is not considered to be significant: assume that an incident 5 eV photon is absorbed in the metal by an electron. This electron interacts with other electrons much faster ($\tau \approx 10^{-15} \text{ sec}$) than with the lattice (via phonons, $\tau \approx 10^{-12} \text{ sec}$), see for example Kittel [Kit96]. This means that the energy of the photon will be spread out over a large volume before it is dissipated to the lattice. This means that one photon cannot cause the temperature to rise significantly, not even locally.

In experiments by Cabrera et al. [Cab49a], UV radiation (100 W/m$^2$, with $h\nu \approx 4 \text{ eV}$) was reported to even double the oxidation rate with respect to natural oxidation. Cabrera argued that the UV light shifts the electron equilibrium and consequently increases the field in the oxide [Cab49a], thereby accelerating the rate of oxidation. Boeve et al. and Song et al. state that UV radiation influences the oxidation process in another way, namely by dissociating oxygen molecules at the surface or in the gas phase, thereby creating O radicals and ozone [Boe00, Son00] which possibly accelerate the oxidation process as suggested in section 3.4.3. To our knowledge, there is no conclusive evidence for either theory so far.

It must be noted that the power delivered by the plasma that is currently under investigation to the sample is about 95 W/m$^2$ (see section 4.3 and the next section), of which only a small fraction is in the form of high energy ($\geq 4 \text{ eV}$) photons. Comparing this with the results of Cabrera’s experiments using much higher radiative powers, this process is considered not to be significant in the plasma oxidation process that is under investigation here.
Figure 3.12: Heat transfer from the plasma through the sample in steady state conditions, which means that the flux is equal in all layers: \( \Phi_p = \Phi_{Al} = \Phi_{Ox} = \Phi_{Si} \)

### 3.4.7 Heating of the surface

In the region between the electrodes, energy is coupled into the plasma via electrons which subsequently transfer kinetic energy to the ions and the background gas by collisions. The background gas is heated, and through the gas the temperature of the sample surface can be increased. In the models discussed in sections 3.2.3 and 3.2.4, an increase in temperature enhances the rate of oxidation as will be shown now. In the logarithmic model the tunneling current in Eq. 3.20 increases if the temperature is increased (see section 1.2.1). In the model of the inverse logarithmic law the temperature enters in the solution of aluminum ions, Eq. 3.23:

\[
\frac{dl}{dt} = N\Omega_{Al}v_{\nu} \exp \left( \frac{-(W - qaE)}{k_BT} \right). \tag{3.42}
\]

Since \( W - qaE \) is positive (see Fig. 3.4) a temperature increase causes an increase in oxidation rate. Hence, in both models an increase in temperature will increase the oxidation rate.

Let us first consider simple conductive heating in order to estimate the temperature rise. During standard operation, described in section 4.3, about 6 W of power is put into the plasma. The sample is at a radius of about 7 cm of the center of the plasma. Assume that the plasma expands in a sphere, hence the flux \( \Phi \) at the sample surface will be

\[
\Phi = \frac{U}{opp} = \frac{U}{4\pi r^2} \approx 95 \text{ W/m}^2. \tag{3.43}
\]

The temperature rise of the surface can be calculated as a simple heat transfer problem, depicted in Fig. 3.12. The flux and temperature gradient are related via

\[
\Phi = -\lambda \frac{dT}{dx}, \tag{3.44}
\]
3.4. Influence of a plasma on oxidation dynamics

where $\lambda$ is the heat conductivity ($\text{Wm}^{-1}\text{K}^{-1}$). We assume steady state conditions which means that the energy flux ($\text{W/m}^2$) is equal in all layers, resulting in linear temperature profiles in each layer. The temperature difference over a layer of thickness $d$ is then given by

$$\Delta T = \frac{\Phi d}{\lambda} \quad (3.45)$$

A sample stack consists of a massive steel substrate-plate (3 mm), a silicon wafer (0.5 mm) with about 3 nm of natural oxide, and on top of that a few nm of metal layer. The substrate-plate is assumed to remain practically at room temperature during the oxidation process. The temperature differences over the silicon ($\lambda = 80 \text{ Wm}^{-1}\text{K}^{-1}$) and silicon dioxide ($\lambda = 1 \text{ Wm}^{-1}\text{K}^{-1}$), are calculated to be only 0.6 mK and $\approx 1 \mu\text{K}$. This means that the temperature increase of the aluminum can be neglected and is not causing the higher oxidation rate of plasma oxidation.

However, the calculation above uses the macroscopic expression for heat transfer, where heat is transferred via many collisions and the temperature is assumed to be homogeneous in the layer. It is obvious that on a micro- or nano-scale this approximation is not valid if a surface reaction delivers a few eV extremely local to only one or a few surface atoms. For example, the energy of a recombination of two O atoms ($\approx 5 \text{ eV}$) is partly transferred to the resulting O$_2$-molecule, the rest can be transferred in the form of heat, i.e. phonons, to the surface. The reaction that delivers the largest amount of energy to the surface is positive ion recombination. The energy delivered is the result of two processes. Partially, it is kinetic energy due to acceleration in the sheath, about 5 to 10 eV. The other part comes from the recombination energy of the positive ion with an electron; for O$_2^+$ this is 12.1 eV and for O$^+$ this is 13.6 eV. Combining these two energies, one ion can deliver very locally an energy of more than 20 eV to surface atoms and electrons, see for example [Mul86]. It must be mentioned that a substantial part of the energy will be converted to kinetic energy of the oxygen molecule, reducing the amount of energy that can be transferred to the surface atom(s).

We suggest that the energy could, for example, assist in dissociation of O$_2$ at the surface, resulting in more O atoms and possibly a higher field.

Figure 3.13: Energy is delivered at spot C, for example by a recombination reaction at the surface. The energy spreads in the oxide towards the metal-oxide interface.
The high packet of energy delivered by an ion could also locally increase the temperature at the metal-oxide interface and assist there in the movement of an Al ion into the oxide. This can be accomplished either by increasing the temperature, increasing the crystal vibration frequency $\nu$, or by increasing the number $N$ of Al ions that is available for movement into the oxide. Recall that $N$ is smaller than the total number of Al interface atoms, see sec. 3.2.4. Probably only atoms that are weakly bound (e.g. at defect sites) are available; a plasma could make also stronger bound atoms available. Since for thermal oxidation a number of $N \approx 10^{19}$ m$^{-2}$ was estimated, which is about a third of the total number of Al ions at the interface, this effect can increase the rate by only a factor of 3 with respect to thermal oxidation.

A rough estimate of the increase in “temperature” at that interface can be made assuming that the energy $Q$ delivered by one ion spreads in the oxide as in Fig. 3.13. Treating this as a macroscopical problem, we assume that the energy spreads out in all directions over half a sphere with radius $r$, as depicted in the figure. The temperature rise of an atom at the heat-front can be calculated from

$$Q(r)\text{per atom} = \frac{Q A}{\pi r^2}$$

(3.46)

where $Q$ is the delivered energy (10 eV), $A$ is the cross-section of one atom ($4 \times 10^{-20}$ m$^2$) and $r$ is the radius of the half sphere. When the heat-front reaches the metal, $r = l$, the temperature rise can be estimated: take $l = 1$ nm and $Q = 10$ eV, then at the metal-oxide interface atoms will have an extra energy of 0.13 eV. This corresponds roughly to the results of Monte-Carlo simulations by Müller [Mul86]. Such a “thermal spike” is comparable to elevating the temperature\(^7\) by 1500 K and could greatly enhance the movement of an Al ion into the oxide (see section 3.2.4). Note that it is in principle not correct to use the term temperature since the system is far from equilibrium.

Therefore, the temperature of a few atoms at the metal-oxide interface of the sample can rise dramatically for a short time. The energy will dissipate very rapidly and can facilitate diffusion of aluminum in the oxide, or, when the aluminum/aluminum-oxide interface is reached, the energy can facilitate the solution of aluminum in the oxide, thereby increasing the oxidation rate directly for a short period of time\(^8\). We will come back to this process in more detail in chapter 7.

\(^7\)1 eV corresponds to 11600 K.

\(^8\)An in-depth Monte-Carlo study on the exact effect of the energy pulse could possibly reveal a growth law with a good correspondence to experiments.
3.5 Conclusions

Two models by Mott and Cabrera that are applicable to the *thermal* oxidation of bulk aluminum have been discussed. In both models, an electric field across the oxide is set up by electrons from the underlying metal, assisting the diffusion of aluminum ions. Two growth laws have been found: the logarithmic law (Eq. 3.21) and the inverse logarithmic law (actually, the Ghez-approximation, Eq. 3.28).

Modifications to this model have been introduced to incorporate the oxidation of ultra-thin layers of aluminum: the possible roles of the limited thickness and of the morphology of the layer (i.e. a grain-structure) have been discussed. It is found that for thin Al layers, the thickness on itself will probably not play a significant role until the oxidation is practically complete. It is likely, however, that the grain-structure that is often observed *does* have an influence: in a model that assumes spherical grains, the work-function will increase significantly as the grain size becomes less than 1 nm in diameter. This implies that the field across the oxide decreases, as will the oxidation rate, as the oxidation process proceeds.

Furthermore, it is discussed how a plasma could have an influence on the oxidation process. It is found that negative charging of the surface due to hot electrons from the plasma on itself will probably not have an influence on the oxidation rate by increasing the field in the oxide. Plasma radiation is also considered to be insignificant in the oxidation process that is investigated in this thesis. Ion implantation as an oxidation process on itself is, at the low ion energies found in this plasma, not significant. Local delivery of energy to the sample by various processes (hot ion bombardement and various recombination reactions) will cause a very local increase of the “temperature”, which, in both models mentioned above, will increase the rate of oxidation. Finally, the presence of excited and “reactive” particles (O\textsubscript{2}, O, O\textsubscript{3}) could influence the oxidation process due to a higher sticking probability and higher electron affinity, resulting in a higher field in the oxide, thereby increasing the rate of oxidation.

Next, experiments on the oxidation dynamics and plasma characteristics are necessary in order to determine what process is responsible for the high rate of oxidation by a plasma as compared to thermal oxidation.
Chapter 4

Experimental Basics and Set-ups

4.1 Introduction

Research on plasma oxidation dynamics implies the use of both surface science methods (i.e. techniques to characterize the layer structure either in real time or after deposition and oxidation) and plasma characterization techniques. A number of techniques from both fields is used, including in-situ differential ellipsometry, X-ray Photoelectron Spectroscopy (XPS), Nuclear Magnetic Resonance (NMR), Low-Energy Ion Scattering (LEIS), Langmuir probes, Two-photon Absorption Laser Induced Fluorescence (TALIF) and actinometry. After the sample preparation and deposition techniques will be addressed, the basics and use of the techniques that are employed will be outlined to some extent. For a better overview, the descriptions of the measurement techniques that were used are divided in two parts. First, the surface science and solid state techniques are described, except for ellipsometry, to which chapter 5 is dedicated. In the second part, the techniques that have been used for characterization of the plasma will be outlined.

4.2 Sample preparation

4.2.1 Substrate preparation

Magnetic tunnel junctions are layered structures, deposited on a very flat substrate (a roughness of only a few tenths of nm rms). The substrate must be non-conducting to eliminate the parasitic current through the substrate, and for this purpose Si(001) wafers with high specific resistivity have been chosen.

Each substrate was cleaned with an ammonia solution or acetone, and
subsequent washing in ethanol, all in a sonic bath. For easy handling in
the UHV-system, the substrates are glued with conducting silver paint onto
stainless-steel sample plates. Sample plates are loaded via a load-lock that
is connected directly to a sputter chamber (see Fig. 4.1). All samples are
flash-heated\footnote{In the load-lock, the sample and sample plate are illuminated by a 1 kW lamp for about
20 seconds at a pressure of 1\times10^{-9} mbar. The temperature of the surfaces is estimated to
be of the order of 500 K.} in order to degas the sample plate and subsequently exposed
for 10 minutes to an oxygen plasma in order to burn away organic residues
of the cleaning process. Additionally, the oxide layer will become thicker
decreasing the parasitic current via the substrate even more.

4.2.2 Deposition of films

The UHV-system that is used for the deposition, oxidation and \textit{in-situ} character-
ation is shown in Fig. 4.1. The films are deposited in a Kurt J. Lesker
sputter chamber (base pressure $< 1\times10^{-9}$ mbar). Using argon DC magnetron
sputtering at 0.010 to 0.013 mbar (7 to 10 mTorr) and 20 Watt, thin films
are deposited with a typical rate of the order of 0.05 nm per second. In
the chamber, 6 targets of different materials (typically a selection of Al, Co,
CoFe, Au, Cr, FeMn, Ta, Ru, Hf, Mg) are present, and the sample can
be moved under each target. By manually controlled opening and closing
of a shutter, materials can be deposited with a resolution of 0.3 seconds,
corresponding to about 0.02 nm. Optionally, a mask can be applied, which
allows for selective deposition on a part of the sample. For \textit{in-situ} analysis of
the deposited layers, a Scanning Tunneling Microscope (STM) and an X-ray
Photo-electron Spectroscopy set-up (XPS) are mounted in a UHV chamber.
The XPS-technique will be described in section 4.4.

4.3 The oxidation set-up

Samples made in the sputter chamber can be transported in UHV (typi-
cally below $10^{-9}$ mbar) via transport rails to a separate, dedicated plasma
chamber in order to maintain a low level of contamination in the sputter
chamber, see figure 4.1. The sample is brought into the chamber on the
conducting sample plate, in a grounded sample holder.

For the growth of thin oxides it is necessary to be able to oxidize repro-
ducibly for short times of the order of 3 to 30 seconds. Because oxidation
systems that use a flowing gas through the chamber always need some time
to set the desired flow and reach the desired pressure in the chamber, a set-
up with a \textit{non-flowing} plasma was developed. A small pre-volume is filled
with a certain amount of gas\footnote{usually oxygen, 99.999\% purity}, which is subsequently let into the chamber
4.3. The oxidation set-up

Figure 4.1: The EUFORAC UHV system for deposition and \textit{in-situ} characterization. The sputter chamber is connected via UHV transportation chambers to the oxidation chamber that includes an ellipsometer, and to a chamber containing an XPS apparatus and an STM.

by pneumatically opening a valve, filling the chamber with a pressure in the range of 1 to 30 Pa. If a high voltage (2 kV) is applied to the electrodes before the gas is let into the chamber, the plasma will ignite practically instantly, creating a stable plasma in less than about 1.5 s (see section 7.3). The method described above implies, however, that the composition of the oxygen gas changes during plasma operation, due to reaction products from the plasma and desorption from the walls.

The plasma is a rotationally symmetric DC glow discharge (see Fig. 4.2), where one electrode, the ring $B$, is at negative potential with respect to the grounded upper electrode, plate $A$. The potential difference can be maximally 2 kV. The power supply is either current or voltage limited. The normal mode that is used is current limiting: set a current, and the power
unit supplies a voltage that is high enough to sustain that current. The
current normally used is 7.5 mA, with a voltage of around 700 V. Ring $C$ is
used as a shield against hot ions sputtered from ring $B$, in other words, the
sample is in its shadow. The plasma can be translated vertically, from close
to the sample to about 50 mm away (the default is a distance of 37 mm
between the sample and ring $C$).

Since the oxidation chamber is heavily used for other research projects
as well, it is inconvenient to frequently vent the chamber for adaptations
for plasma characterization experiments. Therefore a separate, stand-alone
copy of the oxidation chamber was made for easier access and easier plasma-
characterization experiments. It was verified that the copy has essentially
the same properties as the original.

Surface science techniques

4.4 X-ray Photo-electron Spectroscopy

For chemical characterization of the sample X-ray Photo-electron Spec-
troscopy (XPS) is used. XPS is extremely sensitive to the surface (a few
nanometers below the surface) and, because of its potential to distinguish
atoms in different chemical environments, the composition of a layer can be
studied. This section will explain the operation of the XPS technique and
we will focus on the interpretation of the data obtained by XPS.
4.4. X-ray Photo-electron Spectroscopy

4.4.1 The XPS technique

X-rays (Al-Kα, 1486.6 eV) that are incident on the sample ionize atoms down to a few micrometers, usually emitting electrons from the core levels of the atoms. The electrons are ejected with a high kinetic energy that is characteristic of the type of atom it was coming from and the original chemical binding of that electron within the atom:

\[ E_{\text{kin}} = h\nu - E_{\text{bind}} - \Phi_s, \] (4.1)

where \( h\nu \) is the energy of the X-ray photons, \( E_{\text{bind}} \) is the binding energy of the electron, and \( \Phi_s \) is a constant correction term for the work function of the instrument. The binding energy will in general be higher if the atom is chemically bonded. The detector spectrally analyzes the electrons, resulting in a spectrum in which peaks are visible at energies characteristic for orbitals of certain elements in specific chemical surroundings. In Fig. 4.3a, a part of the spectrum of a sample that consists of a partially oxidized aluminum is shown. Two peaks are distinguishable; both originate from the 2p-shell of aluminum. The right peak is caused by metallic aluminum atoms, and the left peak, at a higher binding energy, is due to aluminum atoms that are chemically bonded to oxygen.

![Figure 4.3: An example of an XPS spectrum around the aluminum-2p peaks: a sample with 4.0 nm aluminum, oxidized for 3 seconds. (a) Measurement. (b) Background removed, slightly smoothed and curves fitted.](image)
Chapter 4. Experimental Basics and Set-ups

4.4.2 Quantitative interpretation of XPS spectra

The total intensities (the areas of the peaks) can be used to obtain chemical information, e.g. the stoichiometry of the sample. Since the mean free path of the escaping electrons is typically of the order of the thickness of the layers used in this thesis (a few nm), this involves more than a comparison of peak heights. For a quantitative interpretation of a spectrum a model is needed. A basic model to interpret the XPS spectra measured on typical MTJ samples has been developed and is presented here.

The total intensity $I_A$ of received electrons of a certain transition depends on the concentration and on the depth of the atom: electrons from atoms that lie deeper in the structure have a higher collision probability and will thus not reach the detector, which means they do not contribute to the peak area. Hence an escape depth $\Lambda$ has to be taken into account:

$$\Lambda = \lambda \cos \phi,$$

where $\lambda$ is a material specific escape “distance” and $\phi$ is the angle of the detector with respect to the sample\(^3\). For the metallic and oxidic Al-2p peak, $\lambda$ is 2.03 nm and 1.63 nm, respectively [Sea79]. The total intensity is the sum over all atoms at all depths [Mat85]:

$$I = K \int_0^\infty C(x)e^{-x/\Lambda}dx$$

where $C(x)$ is the atomic concentration (m\(^{-3}\)) at a depth $x$ and $K$ is a constant related to the XPS-set-up. To calculate the total amount of a certain species from the total intensity, the distribution over the $x$-component

\(^3\)In our measurements $\phi$ was 15°.
is needed. In the present case, the aluminum is assumed to oxidize homogeneously: of an Al-layer of a deposited thickness \(d_0\), a thickness \(d_{\text{Al}}\) is left unoxidized as an aluminum oxide of thickness \(d_{\text{ox}}\) is created. The thickness of the remaining Al is connected to the oxide thickness via \(d_{\text{ox}} = 1.275 \cdot (d_0 - d_{\text{Al}})\) (see appendix B.2), as drawn in Fig. 4.4. The concentration of Al atoms in the metallic aluminum is \(C_{\text{Al}}\) and \(C_{\text{ox}} = C_{\text{Al}}/1.275\) in the oxide. The intensity of the oxidic peak is

\[
I_{\text{ox}} = K \int_0^{d_{\text{ox}}} C_{\text{ox}} e^{-x/\Lambda_{\text{ox}}} dx = -\frac{C_{\text{Al}} \Lambda_{\text{ox}}}{1.275} \left( e^{-d_{\text{ox}}/\Lambda_{\text{ox}}} - 1 \right),
\]

and for the intensity of the metallic aluminum peak:

\[
I_{\text{Al}} = KC_{\text{Al}} e^{-d_{\text{ox}}/\Lambda_{\text{ox}}} \int_0^{d_{\text{Al}}} e^{-x/\Lambda_{\text{Al}}} dx
\]

\[
= -KC_{\text{Al}} \Lambda_{\text{Al}} e^{-d_{\text{ox}}/\Lambda_{\text{ox}}} \left[ \exp \left( -\frac{d_0 - d_{\text{ox}}}{\Lambda_{\text{Al}}} \right) - 1 \right],
\]

where the first exponential factor in eq. 4.5 is the attenuation caused by the oxidic top layer. The ratio of the measured total intensities

\[
R = \frac{I_{\text{ox}}}{I_{\text{Al}}} = \frac{\Lambda_{\text{ox}}}{1.275 \cdot \Lambda_{\text{Al}}} \cdot \frac{\exp \left( \frac{d_{\text{ox}}}{\Lambda_{\text{ox}}} - 1 \right)}{\exp \left( -\frac{d_0 - d_{\text{ox}}}{1.275 \cdot \Lambda_{\text{Al}}} \right) - 1}
\]

can be calculated and solved to obtain the oxide thickness \(d_{\text{ox}}\).

In order to calculate \(R\) from the measured spectrum, the areas of the peaks have to be determined. This is done using the available XPS-fitting program, which can automatically subtract backgrounds (of the “Shirley”-type [Fel84], a step-like background), and calculate total peak-intensities. To fit for example the plot in Fig. 4.3a, one needs two peaks of the “Gauss-Lorentz”-type [Fel84]. This is shown in Fig. 4.3b. Each curve has several parameters: the height and width, and parameters to set an asymmetry and a high binding energy tail which is caused by electrons that lost energy in an inelastic collision. The two latter parameters are held fixed for a series of measurements, and were determined for both the metallic and the oxidic peak using a spectrum with a large peak intensity. With these fixed parameters, the program fits the height and width of both peaks consistently and calculates the total intensity (the area under the peak). The exact positions of the peaks are not fixed. They can shift slightly, due to changes in the structure and stoichiometry of the layer.
4.5 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance is a well known technique (see, e.g., Kittel [Kit96]) that is used, for example, for medical imaging of human bodies. As will be explained schematically in this section, NMR can be used to determine small amounts of “damage” (e.g. over-oxidation) to cobalt electrodes. For a more detailed description of the NMR technique, see for example [Str99].

When a magnetic field is applied to an atom with a nucleus with spin $I$, the ground state splits into $2I + 1$ levels, due to the Zeeman interaction [Gri95]. This results in an energy difference $\gamma hB_t$ between two levels, where $\gamma$ is the gyromagnetic ratio of the nucleus and $B_t$ the total field felt by the nucleus. By applying an electromagnetic (EM) field, a transition can be induced between two levels. The nuclear spin system will resonate with this field only when the frequency of the EM field matches the energy difference between the levels:

$$h\omega = h\gamma B_t.$$  \hfill (4.7)

In ferromagnetic materials the spontaneous magnetization gives rise to a large magnetic hyperfine interaction at the nucleus site. The magnitude of the hyperfine field depends on the moment of the atom itself, but also on the number of neighboring atoms and their specific moments. Therefore, an atom in a specific surroundings will have a specific resonance frequency. In a typical NMR experiment the applied magnetic field or the frequency of the EM field is scanned. Atoms in different surroundings will be “selected” and resonate, giving rise to peaks in an NMR spectrum, as shown in Fig. 4.5.

![Figure 4.5: A sample NMR spectrum. The peaks correspond to cobalt atoms in different surroundings; “x NN” denotes Co atoms of which $x$ nearest Co-neighbors are replaced by Cu atoms.](image-url)
4.6 Low Energy Ion Scattering

4.6.1 Principle of LEIS

Low-Energy Ion Scattering Spectroscopy (LEIS, or ISS, Ion Scattering Spectroscopy) is an atomic characterization technique that is even more sensitive to the outermost surface layer than XPS. In a typical LEIS experiment, ions of a noble gas are aimed at a sample with a typical energy of one or a few keV (typically He$^+$ at 3 keV). According to the laws of conservation of momentum and energy, the energy of a backscattered ion (under a certain angle) is characteristic of the mass of the target atom from which it scattered. An energy spectrum of scattered atoms can therefore be interpreted as a mass spectrum of the surface atoms.

Due to the high neutralization probability of He$^+$ ions, the information depth is limited to the outermost atomic layer. By alternatingly removing an atomic layer by sputtering and measuring by LEIS, information can be retrieved about the deeper lying layers. Potentially, depth information on stoichiometry and intermixing at interfaces could be retrieved. However, when doing depth profiling, care must be taken that the sputtering ions, which usually have a higher energy, do not influence the measuring technique by either mixing the layers or by non-uniform sputtering. This might result in an apparent mixing of the atoms in the layers. In order to verify this, a LEIS measurement was performed on a small part of a sample. Afterwards, AFM was performed on the sputtered LEIS-spot as well as on an untouched spot.
4.6.2 Depth profiling using LEIS

Depth profiling was performed on a standard Si / SiOx / Ta(3.5 nm) / Co(4.0 nm) / Al(2.0 nm)+Ox sample in order to gain depth information on stoichiometry and intermixing at interfaces. Helium ions with an energy of 3 keV were used for the LEIS measurement and 3 keV Ne\textsuperscript{+} ions were used for sputtering. Surprisingly, the results of the measurement showed a complete intermixing of the two bottom layers and even some Co in the oxide layer. Furthermore, at the oxide/TaCo interface a lot of intermixing was found. In Fig. 4.6, the nominally deposited layers are compared with the picture that arises from the LEIS measurements.

![Figure 4.6](image1)

**Figure 4.6:** Comparison between the nominally deposited layers (a) and the picture that rises from the LEIS measurements (b). The Ta and Co films are completely mixed, and the interface between the oxide and Co is very rough or intermixed. Some Co was found in the oxide.

It is suspected that the sputtering steps during the LEIS-measurement have caused the intermixing of the layers, and this suspicion was verified by AFM in figure 4.7. It is clear that at the position where layers have been

![Figure 4.7](image2)

**Figure 4.7:** AFM-measurement on Si / SiOx / Ta(3.5nm) / Co(4.0nm) / Al(2.0nm)+Ox. a) Far from the LEIS-area on the sample. The roughness is about 0.3 nm RMS. b) location of sputtering for LEIS. The roughness is about 3 nm RMS.
4.7 MOKE and SQUID

sputtered away, the roughness has increased enormously due to inhomogeneous sputtering. The sputtering inhomogeneity might be caused by differences in sputtering rate between grains and grain-boundaries of the oxide top layer. The large roughness that is created can explain the intermixing that has been observed with LEIS as shown in Fig. 4.8. Unfortunately, this makes LEIS not a suitable technique for depth profiling of our magnetic tunnel junctions.

![AFM-measurement](image)

Figure 4.8: AFM-measurement, showing how the pits created by LEIS cross all layers. In one LEIS-scan, all materials are now visible at the surface and will therefore apparently indicate much intermixing.

4.7 MOKE and SQUID

As mentioned in section 1.2, the two magnetic electrodes of an MTJ should switch independently if a magnetic field is applied. Any magnetic coupling between two layers is undesired but can be created due to magnetic pinholes through the barrier layer. Magnetization loops can supply information on the coupling strength between the two magnetic electrodes in an MTJ and can thus provide information on one aspect of the quality of the barrier layer.

To measure magnetization loops of a layered structure, two experimental set-ups were available. The custom-built MOKE (Magneto-Optical Kerr Effect) is a special version of the differential ellipsometer described in the next chapter, with which the change in polarization due to changes in the magnetization of different layers can be measured [Smi01b]. Of a sample that consists of two or more different magnetic layers, the switching of the individual layers can be observed separately when an applied magnetic field is swept from positive to negative and back.
A SQUID (Super-conducting Quantum Interference Device, a Quantum Design MPMS-5S) can be used to measure magnetization loops as well. A SQUID uses superconducting coils to pick up the magnetic flux from a sample. The magnetization loops can be measured over a temperature range from 5 K to 400 K, allowing for the determination of the nature of the coupling (see chapter 8). The operation of a SQUID is explained in more detail in [Wil97]. The advantage of a SQUID over MOKE is the fact that an absolute value of the magnetic moment can be determined, with a very high resolution. MOKE, however, allows for much faster measurements.

Plasma Techniques

4.8 Langmuir probes

4.8.1 Principle of Langmuir probes

As mentioned in section 3.3, one of the most obvious characteristics of a plasma is the presence of free charged particles, both ionic atoms and molecules, and electrons. This implies that a plasma is able to conduct electricity and that the conductivity will depend on the density and type of charged particles in the plasma. This suggests a potential way of characterization, i.e. via measuring the conductivity of the plasma.

The method that uses the conductivity of a plasma is called Electrical Probes or Langmuir Probes and is very easy to perform: the measurement device consists of one or two electrodes that are inserted in the plasma connected to a voltage source. The conductivity is measured over a range of applied voltages, resulting in an IV-curve from which information can be extracted. As will be shown, Langmuir Probes can potentially provide information on the electron energy and ion densities, and in specific cases on the mass of the ions. However, opposite to the simplicity of the apparatus is the complexity of the modelling and interpretation that is necessary for the extraction of useful information on the plasma. In appendix C the technique of Langmuir Probes will be treated in more detail, limiting this section to a general description and the use of the method.

4.8.2 Double Langmuir probe system

Consider the type of Langmuir probe method that is most commonly used: a double probe system, consisting of two identical electrodes, separated from each other in the plasma. See for a simplified electrical scheme Fig. 4.9.
4.8. Langmuir probes

A sheath region (see sec. 3.3.2) will develop above the surface of each electrode, as in Fig. 4.10a. The electrodes are at a negative potential with respect to the plasma, repelling electrons and attracting positive ions. The net current is zero since the probes are symmetric.

If a voltage is applied to the electrodes, for example positive to probe 1, electrons will be repelled less and positive species will be attracted less. This gives rise to a current through the plasma.

A measurement consists of a sweep of the probe voltage and recording the probe current, see for example Fig. 4.11. From such an IV-characteristic the electron temperature and the ion density can be obtained under some well defined conditions:

1. No ionization occurs in the sheath; the probes do not create their own discharge. This would locally alter the plasma. The applied voltage

![Figure 4.9: The double probe system; $V_a$ and $I_s$ are the applied potential and the measured current.](image)

![Figure 4.10: Potential diagram of double probe system. a) the undisturbed system: two probe surfaces are at a negative voltage with respect to the plasma. The current of electrons towards a probe is equal to the ion current towards the probe. b) A voltage $V_a$ is applied, making probe 1 less negative. The electron current towards this probe is now larger, giving rise to a net current through the plasma.](image)
should therefore not be too high.

2. The electron density is equal to the ion density.
3. The electron temperature is much larger than the positive ion temperature.
4. The typical dimension (radius) of the probe is much larger than the Debye length.
5. There is a Maxwellian distribution of electron and positive ion velocities.

For the full derivation the reader is referred to appendix C, limiting the discussion here to the practical results. From the exemplary IV-characteristic in figure 4.11, the electron temperature can be determined from the slope of the curve around $I = 0$ (the symbols are indicated in the figure):

$$T_e = \frac{I_{s1} - I_{s2} - 1.70S\Delta V_a}{2\left(2 \frac{dl}{dV_a} + S\right)}, \quad (4.8)$$

where $S$ is the average slope of $S_1$ and $S_2$. The ion density can be determined from the electron temperature given by equation 4.8 and the other parameters taken from the figure:

$$n_+ = \frac{\frac{1}{2}(I_{s1} + I_{s2})}{0.6eA_p\sqrt{eT_e/m_+}} \quad (4.9)$$

where $A_p$ is the electrode area ($m^{-3}$), $\hat{T}_e$ is the electron temperature in eV, and $m_+$ is the ion mass, for which an assumption has to be made. In the
4.8. Langmuir probes

In the case of oxygen, it is assumed that molecular ions $O_2^+$ outnumber the atomic ions $O^+$, therefore, $m_+ = 32 \cdot 1.67 \cdot 10^{-27}$ kg.

### 4.8.3 The Langmuir probe set-up

There is a variety of possible Langmuir-probe-configurations that are commonly used in modern experiments. The two main classes are the double probe, as described above, and the single probe, in which the second electrode is formed by the wall of the reactor chamber. Because the “electrode area” of this second probe is very large, and the current scales with surface area, the probe current in a single Langmuir probe experiment will be much larger than in double probe experiments. It was found that in single-probe experiments the probe current can easily become 1 mA (which is 13% of the plasma current) even at moderate probe voltages. Such a high probe current implies a disturbance of the plasma that is unacceptably large, hence the double probe configuration has been chosen.

An important design parameter is the shape of the probe, depending on the experimental conditions. In theory, a spherical probe is most easily modelled since it has no edges (except for the electrical connection) which are difficult to fit into a model. A cylindrical shape is the most simple configuration from a practical point of view, since it consists of nothing more than a conducting wire protruding from an insulating tube. The end of the wire, however, is difficult to model. A planar probe is more difficult to model and interpret due to edge effects. Because of the resemblance with an actual tunnel junction, probes with a flat surface will be used. The electrodes are made by depositing one micrometer of gold on a piece of glass through a mask, leaving two gold areas ($0.25 \text{ cm}^2$) separated by about 10 mm. Gold wires, shielded by ceramic tubes, connect the probes to the voltage source. The probe-plate is placed at exactly the same position where normally a sample is being oxidized.

The IV-measurements were done using a Keithley 2400 Sourcemeter which is a current/voltage source and measurement device in one. IEEE-Communication with a PC allows fast (approximately 5 per second) and flexible measurements. A program sets a voltage and measures the current, and stores the data for later analysis. In order to follow the evolution of the plasma after the ignition, a preset voltage can be maintained while the current as a function of time is measured at 0.2 s intervals.
4.9 Two-photon absorption laser induced fluorescence

In a molecular plasma, for example a discharge containing oxygen, atomic species can play an important role in plasma-solid interfaces since the presence of unpaired electrons implies a large reactivity. Furthermore, other reactive species like ozone (O₃) are possibly created and can play a role in an oxidation process. Laser Induced Fluorescence (LIF) is a direct way of measuring densities of neutral species. The specific case of Two-photon Absorption LIF [Maz00] to measure the density of the ground state of atomic oxygen will be outlined in this section, and it will be shown how ozone can be detected using TALIF simultaneously.

4.9.1 Principle of (TA)LIF

In a LIF-experiment, an atom is excited to a higher state using a laser with the wavelength that fits the transition. After excitation, the atom will radiatively decay, emitting light of a certain wavelength that can be detected. The intensity of this emitted light depends on the density of emitting atoms and the Einstein coefficient for the transition. The lowest excited state of atomic O that can be used for fluorescence is very high, 10.989 eV. Handling of photons of this energy (10.989 eV \( \approx 113.06 \text{ nm} \)) is difficult since these photons are easily absorbed by air [San03]. Instead, two photons of half the energy, 5.49 eV, are used. Since the cross-section for two-photon absorption is much smaller than single-photon absorption, a high-intensity laser beam is needed [Dim84, Han91].

The transition of the \( 2p^4 \left( ^3P_2 \right) \) ground state to \( 2p^33p^1 \left( ^3P_{2,0} \right) \) was chosen, see figure 4.12a. The fluorescence wavelength to the \( 2p^33s \left( ^3S_1 \right) \) state is 844.6 nm. An experiment consists of a scan of the laser frequency around a frequency of interest. Such a scan takes typically 30 minutes. The peak consists of two lines (\( J=2 \rightarrow J=0 \) and \( J=2 \rightarrow J=2 \)) but their separation is only 0.008 cm\(^{-1}\) (at 44315 cm\(^{-1}\)) which cannot be resolved by our set-up. The area is the fluorescence intensity, proportional to the O-density, and the width (FWHM), which is induced by Doppler broadening, is taken to be a measure of the temperature:

\[
\frac{\Delta \nu}{\nu_0} = \left( \frac{8k_B T \ln 2}{mc^2} \right)^{1/2},
\]

where \( \nu_0 \) is the central frequency of the peak, \( \Delta \nu \) is the FWHM of the peak, and \( m \) is the mass of an oxygen atom (2.66 \( \times \) 10\(^{-26}\) kg).
4.9. Two-photon absorption laser induced fluorescence

4.9.2 Detection of ozone via laser-dissociation

In a scheme similar to that of the detection of ammonia [Amo96] and of silane [Miy96], ozone can be detected simultaneously with atomic oxygen. Via laser-dissociation of ozone (the dissociation energy is approximately only 1 eV) hot O is produced:

\[ h\nu + O_3 \rightarrow O + O_2 \]
\[ 5.5 \text{ eV} - 1 \text{ eV} = E_{\text{kin}}^O + E_{\text{kin}}^{O_2} \]

The O atom will have a part of the photon energy minus the 1 eV binding energy. This hot O atom is subsequently measured via the two-photon absorption process. The contributions of O (from the plasma) and O\(_3\) to a TALIF-spectrum can be separated spectrally as shown schematically in Fig. 4.12b): the hot O that is created from ozone will result in a spectral line with a large width due to Doppler broadening, whereas the relatively cold O atoms from the plasma will result in a narrow spectral line. The two parts can easily be separated by fitting two peaks.

4.9.3 Experimental

The TALIF set-up in Fig. 4.13 consists of a high-power laser system of a pulsed Nd:YAG laser (20 Hz repetition rate) which pumps a tunable dye laser with a Coumarin-460 dye. The output pulses are frequency doubled and can be tuned around 225.58 nm (44315.5 cm\(^{-1}\)) with a pulse length of 8 ns. A power of 0.7 mJ per pulse is used, for which it was checked that no saturation takes place.
Chapter 4. Experimental Basics and Set-ups

Figure 4.13: Top view of the TALIF set-up, as described in the text. The pulsed TALIF laser beam is focussed 3 mm above the sample position. Fluorescent radiation is detected perpendicular to this beam.

Using a set of mirrors, the laser light is directed through the plasma chamber. The beam is focussed \((f = 300 \text{ mm})\) in the center of the plasma directly above the sample position as shown in Fig. 4.14. Perpendicular to the laser beam, the light coming from the center of the plasma is projected on a photomultiplier tube (PMT) with a line filter centered at \(\lambda = 850 \text{ nm} \) (FWHM = 20 nm). The intensity of the transmitted laser beam is measured by a photodiode and can be used for normalization, where it is safe to assume that absorption by the plasma is negligible.

All three lines from the ground state \((J = 2, 1, 0)\) have been found since the separations between them are 158 and 69 cm\(^{-1}\), which can easily be resolved by the laser. The splitting of the top level \((J = 0, 2; \text{ see Fig. 4.12a})\)

Figure 4.14: The plasma oxidation set-up where the laser beam is focussed 3 mm above the sample position.
has not been observed. More sensitive measurements may reveal this splitting as well but are not considered relevant for the determination of the oxygen density and temperature.

4.10 Actinometry

The most obvious characteristic of a plasma is that it emits light. This light can be used to obtain a lot of information on the plasma. Atoms and molecules emit light via de-excitation of electrons at wavelengths characteristic for that atom/molecule, which allows for easy identification of the various species present in a plasma [Kui01a]. For example, in 1868, an emission line at 587 nm observed by Janssen and Lockyer in the solar spectrum could not be assigned to any known element on earth. This resulted in the discovery of helium [Wik04] in 1895 by Ramsay.

Besides identification of elements, a spectrum can give more information on properties of the plasma. From emission lines of ions, the degree of ionization can be determined, and under certain circumstances, the ratio between intensities of lines at different wavelengths of one species gives information on the electron temperature in the plasma. Furthermore, the Doppler effect can give rise to a broadening of the lines that is characteristic of the temperature of the emitting atoms [Lie94]. However, interpretation and extraction of quantitative results is only possible if sufficient knowledge (for example, the electron temperature in the plasma, measured by the Langmuir probe technique) of the plasma is already available. In order to get quantitative results, a calibration is necessary, which is normally done by adding a very small known amount of a noble tracer gas like argon. This technique is called actinometry [Pag95] and will be explained in the following sections.

4.10.1 Principle of actinometry

Before atoms can emit light, they have to be in an excited state. In an oxygen plasma, excitation of atoms can occur via various pathways. For the moment, we consider only the most simple excitation process, which occurs via a collision with an electron:

\[ e^- + X \xrightarrow{k_i^e} X_i^* + e^- , \quad (4.11) \]

where \( k_i^e \) is the reaction coefficient. De-excitation of excited state \( X_i^* \) can be radiative:

\[ X_i^* \xrightarrow{A_{ij}} X_j^* + h\nu_{ij}, \quad (4.12) \]
with $A_{ij}$ the Einstein coefficient for the transition from state $i$ to state $j$, or via "quenching", i.e. via a non-radiative collision with species $Q$:

$$X_i^* = Q \xrightarrow{k_Q} X + Q^*,$$

where $Q$ is most likely to be $O_2$ since that is most abundantly present. The reaction coefficient is denoted by $k_Q$. The total flux of emitted photons $I_X$ of a transition $X_i^* \rightarrow X_j^*$ is then written as the ratio between production and loss processes [Pag95]:

$$I_X = C \frac{A_{ij} k_e X_i}{\sum A_{ij} + k_Q [Q]} [X],$$

where $n_e$ is the electron density, $A_{ij}$ is the Einstein coefficient of the transition and $\sum A_{ij}$ is the sum of all transitions from the $i$th level, and $C$ represents an optical factor of the instrument that is unknown but identical for all lines. By comparing the intensity of an oxygen line to the intensity of a line of the added argon, variations in $T_e$, $n_e$ and the factor $C$ can be compensated:

$$\frac{I_{O^*}}{I_{Ar^*}} = \frac{A_{ij}^O k_e^O (\sum A_{ij}^{Ar} + k_Q^O [Q]) [O]}{A_{ij}^{Ar} k_e^{Ar} (\sum A_{ij}^O + k_Q^{Ar} [Q]) [Ar]}.$$

Hence, the ratio of the intensities $I_O/I_{Ar}$ can give the concentration ratio $[O]/[Ar]$ if the other parameters are known or calculated.

The diagram in Fig. 4.15 contains the lines that were chosen for our research. Two oxygen lines were chosen to be compared to one Ar-line that is spectrally close to the two oxygen lines, making sure that the optics for all lines is the same\(^4\).

\(^4\)Which means a comparable absorption through the various parts of the set-up and an identical volume that is measured.
However, in oxygen plasmas an alternative path of creating $O_1^+$ is possible via dissociative excitation [Pag95]:

$$e + O_2 \xrightarrow{k_{de}} O_1^+ + O + e.$$  \hspace{1cm} (4.16)

With this addition, Eq. 4.15 becomes

$$\frac{I_{O_1^+}}{I_{Ar}} = \frac{A_{ij}^O (\sum A_{ij}^{Ar} + k_{Q}[O_2])}{A_{ij}^{Ar} (\sum A_{ij}^O + k_{Q}[O_2])} \cdot \frac{k_e^O[O] + k_{Q}[O_2]}{k_{Q}[Ar]}.$$  \hspace{1cm} (4.17)

in which $k_{de}$ is the reaction coefficient for dissociative excitation. The O density can be easily extracted:

$$[O] = [Ar] \cdot \frac{k_{Q}[O_2]}{k_e^O} \cdot \frac{I_{O_1^+}}{I_{Ar}} \cdot \frac{A_{ij}^{Ar} (\sum A_{ij}^O + k_{Q}[O_2])}{A_{ij}^O (\sum A_{ij}^{Ar} + k_{Q}[O_2])} - \frac{k_{Q}[O_2]}{k_e^O}.\hspace{1cm} (4.18)$$

The reaction coefficients for the reactions in 4.11-4.13 and 4.16 need to be determined. A reaction coefficient, for example for electron excitation, is expressed by

$$k_e^{X_i}(T_e) = \left(\frac{m}{2\pi k_B T_e}\right)^{3/2} \int_0^\infty \sigma_i(v) v \exp\left(-\frac{mv^2}{2k_B T_e}\right) 4\pi v^2 dv$$  \hspace{1cm} (4.19)

where $v = \sqrt{2e/m_e}$ is the electron velocity and $\sigma_i(v)$ is the collision cross-section for excitation to the level $i$, see [Lie94, section 8.5]. Values for the cross-sections $\sigma_X(v)$ for direct excitation and dissociative excitation are taken from [Pag95] and are shown in Fig. 4.16. For this calculation it is assumed that the electrons are thermalized and therefore have a Maxwellian distribution. Using these values the reaction coefficients $k$ are calculated for a range of electron temperatures.

Empirical values for the quenching rates of $O(3P)$, $O(5P)$ and Ar (2p$_1$) in collisions with O$_2$ molecules have been determined in the pressure range of 50 to 266 Pa, from a fit of measurements by Pagnon et al. [Pag95]:

$$\begin{align*}
  k_{3P}[O_2] & = 1.95 \cdot 10^5 p \\
  k_{5P}[O_2] & = 2.63 \cdot 10^5 p \\
  k_{2p1}[O_2] & = 6.09 \cdot 10^4 p
\end{align*}$$

where $p$ is the O$_2$ pressure in Pa. The pressure range used in the experiments in this thesis is from 1 to 40 Pa and therefore the quenching rates might be lower than the values mentioned above.

The values for the Einstein coefficients $A_{ij}$ are summarized in table 4.1.
Chapter 4. Experimental Basics and Set-ups

Table 4.1: The Einstein coefficients for all lines used. The coefficients for total radiative decay happen to be practically equal for all lines involved.

<table>
<thead>
<tr>
<th></th>
<th>$A_{ij} \times 10^8 \text{ s}^{-1}$</th>
<th>$\sum A_{ij} \times 10^8 \text{ s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O($^3\text{P}$)</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>O($^5\text{P}$)</td>
<td>0.369</td>
<td>0.369</td>
</tr>
<tr>
<td>Ar($2p_1$)</td>
<td>0.445</td>
<td>0.445</td>
</tr>
</tbody>
</table>

Figure 4.16: Cross-sections as a function of the electron velocity for direct excitation $\sigma_e^{3P}, \sigma_e^{5P}$ of O and Ar and dissociative excitation $\sigma_{de}^{3P}, \sigma_{de}^{5P}$ of O$_2$. Data from Pagnon et al., ref [Pag95].
4.10.2 The actinometry instrumentation

An image of the plasma is projected via a fiber onto the entry slit of a spectrum analyzer, as shown in figure 4.17. The spatial resolution is determined by the width and height of the entrance opening, which is $\theta 0.2$ mm.

The spectrograph, an Ocean Optics USB2000, is capable of measuring the range 440 nm to 1080 nm with a resolution of 1 nm. By averaging, a spectrum of the light from a certain spot can be obtained in 10 seconds. The intensity of a peak is taken to be the total area of a peak after subtraction of the background which is caused by the environment.

Figure 4.17: The actinometry set-up, using a focusing lens and an Ocean Optics USB2000 spectrograph. The reactor is described in sec. 4.3.
Chapter 5

The Differential Ellipsometry Technique

5.1 Introduction

Knowledge of the oxidation process kinetics of ultrathin metal layers is limited because most useful characterization tools are used in ultra-high vacuum (UHV), like X-ray Photo-electron Spectroscopy (XPS, described in section 4.4), Secondary Ion Mass Spectroscopy (SIMS) and others. The UHV-condition makes those techniques not suitable for real-time investigations on dynamics during the oxidation process at pressures of the order of 10 Pa. Gravimetric measurements using a quartz crystal microbalance (QCM) can be used to study oxidation kinetics via determination of resonance frequencies of the layers with a very high sensitivity (changes of fractions of monolayers can be detected [Fro91]), even in a fluid. In practice, one measurement takes a lot of time due to difficult sample preparation. Furthermore, the choice of substrates is limited which is unwanted in the research of MTJ’s. Wee and coworkers [Wee99a, Wee99b] report on an in-situ technique that uses the increase in resistance of an aluminum strip during oxidation to determine the degree of oxidation. This technique is very powerful in research on MTJs, but has as a major drawback the need for contacting, which is not easily implemented in most vacuum systems.

Ellipsometry, in various forms\(^1\), is a non-destructive and non-invasive technique to characterize layers (in particular layer thicknesses and optical constants). The layers do not have to be grown on a quartz crystal such as in the QCM technique mentioned above, leaving the choice of substrate to the experimenter\(^2\).

\(^1\)E.g. single-wavelength ellipsometry or spectroscopic ellipsometry, see [Lin00]

\(^2\)Although the choice of substrate is not restricted, for practical reasons an absorbing substrate like Si is preferred: the lack of interference effects facilitates the interpretation.
Ellipsometry exploits the fact that light changes its state of polarization upon reflection from an interface between materials with different dielectric properties. In this chapter it is explained how we exploited this technique to measure changes in structure of an aluminum layer during oxidation, and how the validity of the technique is verified using XPS.

5.2 Reflection off a layered structure

Light waves are of electromagnetic origin, consisting of transversal electric and magnetic fields. For interaction with matter, the electric field exerts much bigger forces on electrons than the magnetic field, allowing one to ignore the latter part and consider the electrical field only. This field is chosen to define the polarization of light waves; the magnetic field components can then be deduced using Maxwell’s field equations, see [Gri89]. First, two directions of polarization with respect to the sample are defined (see Fig. 5.1): $E_p$ is the field parallel to the plane of incidence and $E_s$ is the field perpendicular (from the German senkrecht) to the plane of incidence. Of course, for normal incidence, $E_s$ and $E_p$ are the same because no unique plane of incidence can be defined. Any wave can be written as a linear combination of these two and the wave propagation can be calculated for each direction of polarization separately. The electrical field is written as a so-called Jones-vector:

$$\hat{E} = \begin{pmatrix} E_p \\ E_s \end{pmatrix} = \begin{pmatrix} E_p e^{i(\omega t - kx + \phi_p)} \\ E_s e^{i(\omega t - kx + \phi_s)} \end{pmatrix} = \begin{pmatrix} E_p e^{i(\omega t - kx)} \\ E_s e^{i(\omega t - kx + \phi)} \end{pmatrix}, \quad (5.1)$$

where $k$ is the wave vector in the $x$-direction along the propagation direction, $\omega$ is the frequency and $\phi = \phi_s - \phi_p$ is the phase difference between the two polarizations. A linear combination of these two can result in several states of polarization, as sketched in figure 5.2. If the phase difference is zero and the amplitudes are equal, the light is linearly polarized at $45^\circ$, as shown in Fig. 5.2A. If there is a phase difference, for example, $E_s$ lags behind $E_p$ by
5.2. Reflection off a layered structure


π/2 in Fig. 5.2B, the resulting light will be (clockwise) circularly polarized. A difference in amplitude between the two components results in a rotation, as in Fig. 5.2C. A combination of a phase difference and a difference in amplitude will give a rotated ellipse as in the right-most picture, D. The ratio between the p- and s-components can be written as

\[ \chi = \frac{E_p}{E_s} = e^{i \Delta \tan \psi}, \]  

where \( \Delta \) and \( \psi \) represent the ellipticity and the rotation, respectively.

The natural quantity of a light wave that can be measured is the intensity. The intensity \( I \) of a light wave with a certain Jones vector is given by

\[ I \propto E_p E_p^* + E_s E_s^*, \]  

where the asterisks denote the complex conjugate.

In a layered structure, an incident ray of light is reflected and transmitted at each interface between layers. This process is different for s- and p-polarized light. The reflection and transmission coefficients for the s-component are given by [Yeh88]:

\[ r_s = \frac{n_1 \cos \Theta_1 - n_2 \cos \Theta_2}{n_1 \cos \Theta_1 + n_2 \cos \Theta_2} \quad \text{and} \quad t_s = \frac{2n_1 \cos \Theta_1}{n_1 \cos \Theta_1 + n_2 \cos \Theta_2}, \]  

and for the p-component:

\[ r_p = \frac{n_1 \cos \Theta_2 - n_2 \cos \Theta_1}{n_1 \cos \Theta_2 + n_2 \cos \Theta_1} \quad \text{and} \quad t_p = \frac{2n_1 \cos \Theta_2}{n_1 \cos \Theta_2 + n_2 \cos \Theta_1}, \]  

where \( n_i \) is the index of refraction of layer \( i \), and \( \Theta_i \) is the angle of the light ray in layer \( i \) with the surface normal. \( \Theta \) can be calculated using

\[ \frac{\sin \Theta_1}{\sin \Theta_2} = \frac{n_2}{n_1}. \]
Chapter 5. The Differential Ellipsometry Technique

To calculate the reflection from a multilayer-stack as in Fig. 5.3 a matrix-formulation is used. The electrical field in each layer, satisfying Maxwell's equations, is given by:

\[ E = E_0 e^{i(\omega t - \beta z)} = E(x) e^{i(\omega t - \beta z)}, \]  

where the $z$-dependent part has been split off; $\beta$ is the $z$ component of the wave-vector. Now $E(x)$ can be written as a sum of two waves, one travelling to the right and one to the left:

\[ E(x) = R e^{-ik_{x1}x} + L e^{ik_{x1}x} = A(x) + B(x). \]  

The following equations are treated in terms of $p$-polarized light; for $s$-polarized light similar relations hold. If the A and B components in a layer are written as a column-vector, the equation that relates the fields at the left and right of an interface, for example between layers 0 and 1, is given by (see [Yeh88], page 103, 104):

\[ \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = D_{12p} \begin{pmatrix} A'_1 \\ B'_1 \end{pmatrix}, \]

where

\[ A'_i = A(x_{i} + \delta x), \quad \text{and} \quad A_i = A(x_{i+1} - \delta x). \]

The relation between fields at the left and right boundaries of a layer is:

\[ \begin{pmatrix} A'_1 \\ B'_1 \end{pmatrix} = P_1 \begin{pmatrix} A_1 \\ B_1 \end{pmatrix}. \]
5.2. Reflection off a layered structure

In these equations, \( D_{12p} \) is a transmission matrix for the \( p \)-direction, given by

\[
D_{12p} = \frac{1}{t_{12p}} \begin{pmatrix} 1 & r_{12p} \\ r_{12p} & 1 \end{pmatrix},
\]

(5.11)

where \( r_{12p} \) and \( t_{12p} \) are in this case for \( p \)-polarized light. \( P_l \) is the propagation matrix for both polarization directions for layer \( l \):

\[
P_l = \begin{pmatrix} e^{ik_{lx}d_l} & 0 \\ 0 & e^{-ik_{lx}d_l} \end{pmatrix},
\]

(5.12)

with \( k_{lx} \) the wave vector in the \( x \)-direction in layer \( l \):

\[
k_{lx} = \frac{n_l \omega}{c} \cos \Theta_l.
\]

(5.13)

The fields in any two layers can be related by combining the matrices. For example, the relation between \( A_0, B_0 \) and \( A_2, B_2 \) is:

\[
\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = D_{12p} \begin{pmatrix} A'_2 \\ B'_2 \end{pmatrix} = D_{12p} P_2 \begin{pmatrix} A_2 \\ B_2 \end{pmatrix},
\]

(5.14)

For a structure with more layers, the total matrix \( M_p \) is found by multiplication:

\[
\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = M_p \begin{pmatrix} A_{sub} \\ B_{sub} \end{pmatrix}.
\]

(5.15)

The case where, in Fig. 5.3, a beam of light is incident from the left is interesting. \( B_s \) is set to zero since there is no wave incident from the right and the total reflection coefficient for the \( p \)-direction can be calculated:

\[
r_{tot,p} = \begin{pmatrix} B_0 \\ A_0 \end{pmatrix}_{B_{sub} = 0},
\]

(5.16)

which can be related to the matrix-elements of \( M_p \):

\[
\begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} M_{11p} & M_{12p} \\ M_{21p} & M_{22p} \end{pmatrix} \begin{pmatrix} A_{sub} \\ 0 \end{pmatrix} \implies A_0 = M_{11p} A_{sub} \quad B_0 = M_{21p} A_{sub}
\]

(5.17)

Therefore, the total coefficient of reflection for the \( p \)-polarization, in terms of matrix-elements, is

\[
r_{tot,p} = \frac{M_{21p}}{M_{11p}}.
\]

(5.18)

The same procedure can be followed in order to find the total reflection coefficient \( r_{tot,s} \) for \( s \)-polarized light.

The theory outlined here results in expressions for the reflection coefficients of a layered structure, with which in principle the change in polarization of an incident laser beam can be calculated. Using these results, a technique based on measuring small changes in the polarization of the laser beam has been developed and will be outlined in the next sections.
5.3 Analysis

In order to observe small changes in layers, for example due to oxidation of the top layer(s), we have developed a *differential ellipsometer*. In this section, we explain the theory behind the general set-up that is shown schematically in Fig. 5.4. A polarized laser beam is incident on the sample which induces a change in the polarization of the reflected light as described in the previous section. The reflected laser beam passes a photo-elastic modulator (PEM) and is finally analyzed by a second polarizer and the intensity is measured by a detector. The modulation \((f = 50 \, \text{kHz})\) induced by the PEM is used in combination with a lock-in technique in order to filter out noise and fluctuations. Changes in the structure, due to oxidation, will be reflected by changes in the lock-in signal. Next, the set-up will be treated in more detail.

In the set-up, polarized light at an angle \(\alpha\) (with respect to the plane of incidence) is incident on a sample at an angle of 45°. This polarization is created by a polarizer under an angle \(\alpha\):

\[
P_\alpha = \begin{bmatrix} \cos^2(\alpha) & -\cos(\alpha)\sin(\alpha) \\ -\cos(\alpha)\sin(\alpha) & \sin^2(\alpha) \end{bmatrix},
\]

and the polarization of the laser beam is represented by a Jones vector:

\[
\mathbf{L}_\alpha = \begin{bmatrix} \cos(\alpha) \\ \sin(\alpha) \end{bmatrix}.
\]

Normalization factors are left out for reasons of clarity. A sample introduces a reflection as discussed above, with a Jones matrix \(S\), written in a convenient form:

\[
S = \begin{bmatrix} r_p & 0 \\ 0 & r_s \end{bmatrix} = r_p \begin{bmatrix} 1 & 0 \\ 0 & S_1 + iS_2 \end{bmatrix},
\]

\[
\text{Figure 5.4:} \quad \text{The general set-up for a differential ellipsometer. A laser beam is polarized at an angle } \alpha, \text{ reflected off the sample and guided through a modulator (PEM) and finally analyzed by a second polarizer and detector.}
\]
where \( r_p \) and \( r_s \) are the reflection coefficients from Eq. 5.18 for \( p- \) and \( s- \) polarized light, respectively. The reflected light passes through a photoelastic modulator (PEM) and a polarizer. A PEM is a device with a periodically modulated index of refraction for light polarized along one of its axes. The Jones-matrix for this device is

\[
M_{\text{PEM}} = \begin{bmatrix} e^{iA} & 0 \\ 0 & 1 \end{bmatrix} \quad \text{with} \quad A = A_0 \cos(\Omega t).
\] (5.22)

The PEM is set to an angle of \( 45^\circ \) with respect to the plane of incidence. A rotation of \( 45^\circ \) can, in terms of Jones matrices, be handled by a transformation to a rotated coordinate system and back. A rotation by an angle \( \phi \) is given by the matrix

\[
R_\phi = \begin{bmatrix} \cos(\phi) & \sin(\phi) \\ -\sin(\phi) & \cos(\phi) \end{bmatrix}.
\] (5.23)

The matrix of a \( 45^\circ \) rotated PEM is therefore

\[
M_{\text{PEM@45}} = R_{-45} \cdot M_{\text{PEM}} \cdot R_{45}.
\] (5.24)

The final polarizer\(^3\) is set to \( 0^\circ \) with respect to the plane of incidence. The resulting light is represented by the total matrix:

\[
P_0 \cdot M_{\text{PEM@45}} \cdot S \cdot L_\alpha.
\] (5.25)

The resulting matrix is rather complicated and will not be shown here. The intensity of this light is of interest, using Eq. 5.3:

\[
I = \frac{1}{2} |r_p|^2 \left[ (1 + \cos A) \cos^2 \alpha + (1 - \cos A)(S_1^2 + S_2^2) \sin^2 \alpha + 2S_2 \sin A \cos \alpha \sin \alpha \right].
\] (5.26)

Here use is made of \( e^{iA} = \cos A + i \sin A \). The \( \cos A \) and \( \sin A \) terms in Eq. 5.26 (with \( A = A_0 \cos \Omega t \)) can be expanded using

\[
\cos A = J_0(A_0) + J_2(A_0) \cos(2\Omega t) + J_4(A_0) \cos(4\Omega t) + \ldots
\]
\[
\sin A = J_1(A_0) \cos(1\Omega t) + J_3(A_0) \cos(3\Omega t) + \ldots,
\] (5.27)

where \( J_i \) is the \( i^{th} \) Bessel function of the first kind. Neglecting the higher order harmonics above \( 2\Omega \), the intensity can be divided into a “dc” part, a “1f” part and a “2f” part:

\[
V_{\text{dc}} = |r_p|^2 \left[ (1 + J_0(A_0)) \cos^2 \alpha + (1 - J_0(A))(S_1^2 + S_2^2) \sin^2 \alpha \right].
\] (5.28a)

\(^{3}\)This polarizer is often called analyzer because of its function.
These three parts of the intensity can be detected separately by a lock-in technique. The amplitude of the modulation of the PEM, \( A_0 \), can be chosen freely. It is usually set to a maximum of one of the Bessel functions in order to maximize the relative strength of the corresponding signal\(^4\).

When changes in the structure of the sample are introduced (e.g., by oxidation of the layer, or by scanning the laser spot over a non-homogeneous sample), the reflection coefficients \( r_p \) and \( r_s \) (and \( S_1 \) and \( S_2 \) as well) will change and the 1f- and 2f signals will vary accordingly.

In order to increase the sensitivity to changes in the layer structure, the angle of the polarizer \( \alpha \) can be chosen such that the 2f-signal is zero at the start of a measurement, which means that a more sensitive range of the detector can be chosen, resulting in a better signal-to-noise ratio. The angle for which \( V_{2f} = 0 \) is easy to determine:

\[
\alpha_{2f=0} = \tan^{-1} \left( \frac{1}{S_1^2 + S_2^2} \right)^2.
\]

It can be shown that, at this setting, the absolute change in signal is larger as well, resulting in an even better signal-to-noise ratio.

For examining the behavior of the 1f and 2f signals as a function of layer structure, we assume that we scan the ellipsometer laser over a sample that consists of a single layer of Al (on an Si substrate). The Al thickness varies linearly over the sample area, as sketched in Fig. 5.5a, structure A. Using a simulation program, the reflection coefficients for both s- and p-polarized light for a certain structure can be computed. The corresponding 1f and 2f signals as a function of Al thickness are shown in the graph. It is found that the 1f and 2f signals vary practically linearly with the thickness of the aluminum layer. Structure B in Fig. 5.5a resembles an oxidation process: Al is converted to Al\(_2\)O\(_3\), with a constant rate. Thus, the only difference with structure A is the extra Al\(_2\)O\(_3\) layer. The corresponding 1f and 2f signals are shown in Fig. 5.5b as well. It is observed that the 1f signals are different, but the 2f signals are practically identical; the 2f signal is clearly not sensitive to an oxidic layer on top of the structure.

From this it is concluded that the 2f signal is sensitive to the metallic layers only, which facilitates the interpretation of a measurement during the oxidation of a layer of aluminum. The 1f signal reflects changes in both the metallic and the non-metallic parts of a sample. If the structure becomes more complex (i.e. more layers are added), the relation can become less

\[^4\]J\(_1\) is maximal at \( A_0=1.94 \), J\(_2\) is maximal at \( A_0=3.05 \).
5.3. Analysis

$$d_{Al} = 2\, \text{nm}$$

$$d_{Al} = 2\, \text{nm}$$

$$d_{Al} = 2.5\, \text{nm}$$

Figure 5.5: a) Simulations of the 1f- and 2f- signals as a function of Al-thickness of two samples, as explained in the text. Structure A consists of a ‘wedge’ of aluminum of 2 nm at the thickest part. Structure B has the same Al wedge from structure A, but now with an extra $\text{Al}_2\text{O}_3$ wedge of 2.5 nm on top, resembling an oxidation process in which Al is converted to $\text{Al}_2\text{O}_3$.

linear. For the structures encountered in this thesis (for instance a structure consisting of Si/SiOx/Ta/Co/Al) it has been verified that the relation between the Al thickness and the 2f signal is linear within 5%.

The absolute signal amplitude is reduced by the absorption in metallic layers: as the total thickness of the metallic layers increases, the signal amplitude decreases. For instance, in simulations it is found that the oxidation of 1 nm Al of a deposited thickness of 10 nm Al will result in a three times lower 2f-signal than if the deposited Al layer was only 3 nm.

We conclude that the 2f signal is sensitive only to changes in the thickness of metallic layers (i.e. absorbing layers) and is insensitive to non-metallic materials.
5.4 The \textit{in-situ} differential ellipsometer set-up

In Fig. 5.6, the set-up that was designed and used for the \textit{in-situ} measurements is drawn schematically. Light from a 3 mW HeNe laser (Melles-Griot, $\lambda = 632.8$ nm) is polarized at a certain angle $\alpha$ (with respect to the plane of incidence on the sample) and is aimed through a viewport (at 90°) into the oxidation chamber at a sample, under an angle of approximately 45°. From there, the light is reflected from an internal mirror, through a viewport\(^5\) at 45° via another mirror to the rest of the set-up: a PEM and an analyzer, and, via a focusing lens ($f \approx 50$ mm), onto a photodiode detector. The two mirrors rotate the coordinate system by 45°, which means that the PEM is at 45° and the analyzer is at 0° with respect to the sample.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_6}
\caption{The \textit{in-situ} Differential Ellipsometer set-up, mounted on the oxidation chamber. P: polarizer, S: sample, M1, 2: mirrors, A: analyzer, L: lens, D: detector. The laser enters the chamber via viewport W1, perpendicular to its surface. The laser beam exits the chamber via viewport W2 under an angle of 45°.}
\end{figure}

Since the angle of incidence on the entrance viewport is 90°, it does not affect the polarization\(^6\), assuming that the window is homogeneous. The angle of incidence on the second window is 45°, and the state of polarization

\footnote{The existing oxidation chamber did not have the possibility to mount the exit viewport at 90°.}

\footnote{If the angle of incidence is 90°, no unique plane of incidence can be determined, and \textit{s} and \textit{p} polarized light are identical.}
of the light can therefore be changed. This is neglected for the moment. Both mirrors are mounted such that the induced changes in polarization effectively cancel. Any influence on the polarization caused by the lens is of no importance since after the laser beam has passed the analyzer, only the intensity is relevant.

The electrical diagram is given in Fig. 5.7. The PEM, which modulates the laser light at 50 kHz, passes a reference signal to the Lock-In Amplifier (LIA, EG&G model 7265). Of the modulated intensity registered by the detector, both the double-frequency (2f)-component and the DC-component (after low-pass filtering) are separated by the LIA. By adding a second LIA (EG&G model 5201), also the 1f-component can be measured. Both signals are read by a computer via GPIB (IEEE) communication, which, in the current set-up, allows measuring rates up to 50 measurements per second. In the next section, the validity of the technique will be verified, as well as the influence of the laser on the sample and the influence of the plasma on the ellipsometry technique.

5.5 Validation of the technique

A typical ellipsometry measurement during an oxidation process is shown in Fig. 5.8. The general procedure, described in more detail in section 4.3, is as follows. Preceding the start of a measurement, a voltage is applied to
Figure 5.8: Ellipsometry during the oxidation of Si / SiO$_x$ / Ta(3.5 nm) / CoFe(4.0 nm) / Al(2.0 nm). Standard oxidation conditions were used: the plasma power is 6 Watt, the pressure is 10 Pa. The inset shows the first seconds of the oxidation process after the plasma is started.

the plasma-electrodes and the chamber is sealed by closing the valve to the pumping system. The polarizer is rotated to set the initial 2f-signal to zero at the start of the measurement.

In order to be able to link the 2f-signal to the simulations and to compensate for the small differences in alignment that exist between measurements, a calibration is performed: the polarizer is shortly rotated by $0.5^\circ$ and $\Delta 2f_{0.5}$ is measured. The complete measurement is afterwards normalized by division by $\Delta 2f_{0.5}$.

Generally, between the calibration and the actual oxidation start ($t < 0$ s) a small change in the 2f signal is already observed. This corresponds to thermal oxidation due to the background oxygen pressure that rises to about $10^{-5}$ Pa. This will be discussed in more detail in section 6.2.

At time $t = 0$ s, the chamber is quickly (within $\approx 1$ s) filled with oxygen gas up to a specific pressure around 10 Pa and the plasma ignites immediately, as described in section 4.3. At the start of the plasma ($t = 0$ s), an extremely fast initial oxidation is observed in Fig. 5.8. As the oxide becomes thicker, the oxidation rate decreases rapidly. As shown before, the 2f-signal corresponds with a high degree of accuracy to the amount of aluminum that is converted to oxide.

Next, the reliability and predictability of the technique will be investigated by comparing the optical measurements with an established technique, X-ray Photo-electron Spectroscopy (XPS). XPS, described extensively in
5.5. Validation of the technique

Figure 5.9: (a) XPS-spectra of the stepwise oxidation of a layer of 4 nm aluminum. (b) Ellipsometry data compared with oxide thickness, extracted from the XPS spectra of the same sample. The uncertainty in the fraction stems from the peak fitting procedure.

section 4.4, is a chemical characterization technique with which Al in metallic aluminum and aluminum oxide can be discriminated, and the amount of unoxidized aluminum can be determined quantitatively. In order to verify the validity of the ellipsometer technique, we set up the following experiment using XPS; see also [Kne01]. A sample of 4 nm Al was oxidized stepwise for short periods while measuring with ellipsometry. In between the steps, the sample was transferred to the XPS chamber (see Fig. 4.1) and XPS-spectra around the Al-2p peak at 73 eV of the sample were measured. The ellipsometry measurements thus obtained were plotted together in one graph. The XPS-spectra, shown in figure 5.9a, were fitted, and the oxidized fraction of the layer was calculated after each oxidation step, as described in section 4.4.

The ellipsometry-data and the thicknesses that were extracted from the XPS-spectra are plotted together in figure 5.9b. The ellipsometry data were rescaled and shifted along the y-axis such that at $t = 0$ s and at $t = 721$ s the two data sets overlap. In between, one can see that the ellipsometry data correspond very well to the XPS data. The ellipsometry data seem to be slightly lower than the XPS measurement. This small difference between the two data sets is ascribed to a small amount of extra oxidation of the

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7It must be noted that if the plasma is restarted in order to continue the oxidation process, a small delay (of at most a few seconds) that becomes larger with each oxidation step is observed.
layer during pump-down of the oxidation chamber and transport to the XPS chamber. The uncertainty in the XPS-data is a result of the peak fitting procedure and the uncertainty in the escape depths of the electrons in the oxide and metal, see appendix B.2. It is observed that already a small but significant amount of aluminum, 0.4 nm Al (corresponding to \( \approx 0.5 \) nm Al\(_2\)O\(_3\)) has already been oxidized before the actual oxidation experiment is started. It is also observed that the oxidation is not complete after 800 seconds of oxidation.

As mentioned above, before the start of the measurement, a calibration is done to be able to compare the data with simulations in order to directly extract information on the progress of the oxidation. Unfortunately, the simulation has proven to be extremely sensitive to the values of all optical constants of the layer structure as well as on the thicknesses of all layers. Since for these thin layers the exact optical constants probably deviate from values of bulk samples, it has been found to be difficult to quantitatively match simulations with the data. Therefore, calibrations at the beginning of a measurement will be used only to normalize measurements on identical samples, in order to eliminate differences in alignment in a series of experiments.

As explained in section 5.3, using Fig. 5.5, the 1f-component can provide extra information, specifically on the thickness of the oxide. However, it has been found that in the current set-up the changes in the 1f-signal due to the oxidation process are small compared to the initial value of the 1f-signal. Noise and fluctuations, probably caused by vibrations in the UHV system, inhibit a reproducible registration of the 1f signal. The 1f-signal is therefore not used in this thesis although it can potentially provide useful additional information on the tunnel barrier\(^8\).

We conclude from these data that the real-time *in-situ* ellipsometer can be used to adequately follow the oxidation dynamics. However, it is possible that the laser has an influence on the oxidation process, for instance by heating the sample surface and thereby accelerating the oxidation process. Furthermore, the charged particles in the plasma could have an influence on the polarization of the laser beam. These complications will be addressed below.

**Influence of the laser on the oxidation process**

It is often stated that ellipsometry is a non-intrusive technique. In our case this would mean that the laser does not influence the plasma nor the oxidation process. However, several mechanisms can be thought of: for instance,

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\(^8\)By addition of a quarter-wave plate after the first polarizer, it is possible to remove the offset on the 1f-signal as well. In this research, this has not successfully been performed.
via direct heating of the sample the oxidation process could be accelerated (section 3.4.7). Light assisted oxidation, as described in section 3.4.6, might occur as well. Therefore, it is of importance to rule out any influence. An experiment has been set up to verify this. Two identical samples were made in the regular way (2.0 nm Al on Si/SiOx), one of which was oxidized and measured normally using the optical technique, that is, with constant illumination of the sample by the laser. The other sample was oxidized in exactly the same conditions, but the laser was covered by a shutter which was periodically opened for only short periods of measuring. The measurements are compared in Fig. 5.10. To a very good approximation, the two measurements overlap, and from this we conclude that the influence of the laser is negligible, making our ellipsometer a truly non-intrusive technique.

\[
\epsilon_p = 1 - \frac{\varepsilon_p^2}{\varepsilon_r^2},
\]

(5.30)
where $\omega$ is the angular laser frequency ($3 \times 10^{15}$ s\(^{-1}\)) and $\omega_p$ is the plasma frequency, defined as

$$
\omega_p = \left( \frac{e^2 n_+}{\varepsilon_0 m_e} \right)^{1/2},
$$

(5.31)

where $n_e$ is the electron density which is assumed to be equal to the ion density $n_+$, and $m_e$ is the electron mass ($m_e \approx 9 \times 10^{-31}$ kg). The effect is usually only significant at very high electron densities and if a low-frequency electromagnetic field is used. In this glow discharges, the electron density is of the order of $10^{15}$ m\(^{-3}\) (see section 7.8) and the plasma frequency is about $1.7 \times 10^9$ s\(^{-1}\). This means that the dielectric constant is approximately $1 - 3 \times 10^{-13}$ and that the influence is therefore insignificant in our ellipsometer.

## 5.6 Conclusions

Summarizing, we conclude that the differential ellipsometer developed here is ideally suitable for observing the oxidation process in real-time with high temporal and depth resolution. It is found to be non-intrusive and no influence of the presence of the plasma on the ellipsometry technique is to be expected. In oxidation experiments, the ellipsometer response can be correlated linearly to the amount of oxidized aluminum.
Chapter 6

Experiments on Oxidation Dynamics

6.1 Introduction

In the first part of the investigation of the oxidation process, contained in this chapter, we neglect for the moment the exact influence of the plasma, which will be discussed in chapter 7. Attention is focussed here on the determination of the oxidation process steps and the dependence of the oxidation dynamics on the sample itself. The correct model for thermal oxidation is determined and the effect of granular structure of the aluminum layer is investigated. A method using the in-situ ellipsometer is developed to determine in real-time when over-oxidation of sub-nanometer Al layers takes place.

6.2 Sticking coefficient of oxygen on Al surfaces

In practice, at very low pressures, the rate of oxidation is limited by the sticking coefficient and the flux of oxygen arriving at the surface, as explained in section 3.2.2. This occurs, as has been mentioned in section 5.5, as soon as the oxidation chamber is sealed from all pumps and the pressure rises quickly to about $10^{-5}$ Pa ($10^{-7}$ mbar). Some small amount of oxidation will occur, which is shown in Fig. 6.1. A constant oxidation rate, indicated by the straight line, of about $(4 \pm 0.2) \cdot 10^{-4}$ nm/s is observed\(^1\). This corresponds to $1.4 \cdot 10^{16}$ O\(_2\) molecules/m\(^2\)s (see section 3.2.2). Assuming that the pressure rise to $10^{-5}$ Pa is solely due to oxygen coming from the walls from previous oxidation experiments, the flux of oxygen molecules towards

\(^1\)The measurement (Fig. 5.8) was calibrated with an accuracy of about 5% by assuming that the 2f-signal after 200 seconds corresponds to full oxidation, as this is the optimal oxidation time for actual junctions (not published).
the sample is $2.7 \cdot 10^{17}$ m$^{-2}$s$^{-1}$ (Eq. 3.3). Thus it is found that apparently about 5% of the oxygen flux is consumed at the sample. This implies a sticking or reaction coefficient of 0.05±0.003, which is substantially higher than the value of 0.005 derived by Osterlund [Ost97] on Al(111) crystals. This strongly suggests that the poly-crystalline or amorphous nature of the layers grown here influences the sticking/reaction coefficient of oxygen dramatically.

### 6.3 Thermal oxidation of thick aluminum

Before discussing the influence of the plasma or the thickness of the layer, it is essential to know which of the two basic models for thermal oxidation outlined in chapter 3 is valid for the aluminum layers under investigation here. The oxidation rate in the logarithmic model (section 3.2.3) was determined by the rate of tunneling of electrons through the growing oxide, resulting in:

$$ l = l_0 \ln \left( \frac{O_x}{l_0} t + c \right). $$

where $l$ is the oxide thickness, $t$ is the oxidation time and the other parameters are constants as explained in chapter 3. In the inverse logarithmic model (section 3.2.4), the oxidation rate is determined by the rate of movement of aluminum ions into the oxide, assisted by the field which is dependent on the oxide thickness. This results in

$$ \frac{l_1}{l} = -\ln \left( \frac{t + \tau}{l^2} \right) - \ln(l_1 u). $$

![Figure 6.1: Thermal oxidation, before the gas is let into the chamber. The pressure is about $10^{-5}$ Pa, the oxidation rate is about $4 \cdot 10^{-4}$ nm/sec.](image)
6.3. Thermal oxidation of thick aluminum

In order to obtain information about the basic oxidation model, without the influence of a plasma or interfaces, as described in sections 3.2.3 and 3.2.4, we performed a natural oxidation experiment (in 10 Pa at room temperature) on a thick layer of aluminum. The deposited Al thickness used must be chosen such that the influence of any interface can be neglected, hence the Al thickness must be larger than 2 nm [Cab49a]. As mentioned in section 5.3, the layer thickness should not be too large in order to obtain a good signal to noise ratio. It is estimated that an aluminum thickness of 7 nm is large enough to be able to ignore the influence of the non-aluminum buffer layer (3.5 nm of tantalum) but the total thickness is still small enough for the signal amplitude to be acceptable.\(^2\)

In Fig. 6.2 the measurement is displayed semi-logarithmically. A straight line should be observed if the oxidation follows the logarithmic law from Eq. 6.1. We observe that the middle part of the measurement is a straight line, but that deviations appear at the start of the measurement and at longer oxidation times. The deviation at short oxidation times, the first second, is partially due to the finite speed of the gas-inlet and the response time of the ellipsometer, and partially due to the fact that the logarithmic model is not valid for the oxidation of the first monolayers. At longer time scales, above 100 seconds, the deviation from the straight line implies a

\(^2\)It was verified by simulations that for this experiment the ellipsometer signal is directly linear with the oxidized thickness within 1%. 

\[ \text{Figure 6.2: Ellipsometry during the natural oxidation of Si/SiO}_2/Ta(3.5 \text{ nm})/Al(7.0 \text{ nm}). \text{ Natural oxidation conditions: pure O}_2 \text{ at 10 Pa, no plasma. The data are plotted semi-logarithmically, the inset shows the raw data. The measurement data should lie along the dashed line if the oxidation followed the logarithmic law.} \]
Figure 6.3: The data from the natural oxidation experiment, shown in the inset in Fig. 6.2, are plotted semi-logarithmically as $1/l$ versus $(t+\tau)/l^2$. The parameter $\tau$ was taken to be 0.2 seconds, see sec. 3.2.4.

In Fig. 6.3 the data are plotted as $1/l$ versus $\log(t/l^2)$, where $l$ is the amount of oxidized aluminum. This should result in a straight line if the Inverse Log-model is valid according to the approximation of Ghez, as mentioned above. Again, the initial oxidation deviates from a straight line, partially due to the fact that the inverse Log-model is not valid for the first monolayer, and partially due to the finite time of gas inlet. For larger times, a perfect match is found. From this observation we conclude that the thermal oxidation of our aluminum films follows the inverse-logarithmic-model of Cabrera [Cab49a].

From the fit above we can deduce values for the parameters $W$ and $V$ in the model and compare them to the values earlier obtained by Cabrera from temperature dependent measurements (section 3.2.4). The parameters $u$ and $l_1$ in the approximation of Ghez are found to be $1.47 \cdot 10^{-20}$ m/s and $1.60 \cdot 10^{-8}$ m, respectively. From $l_1 = qaV/k_BT$ and $u = u_0 \exp(-W/k_BT)$ and assuming for $a$ and $u_0$ Cabreras values of 0.35 nm and 100 m/s, respectively, we find for the solution energy $W$ a value of 1.3 eV and for the oxide voltage $V$ a value of 1.18 V. Both are reasonable values, but lower than found by Cabrera: $W = 1.8$ V and $V = 2.0$ V. Our lower value of the solution energy $W$ and oxide voltage $V$ is probably due to the morphology of the sputtered aluminum. For instance, the roughness of the surface and Al/Al$_2$O$_3$ interfaces could influence $V$ and the grain-like structure will probably create a variation of $W$ over the sample.
Now that the basic model for natural oxidation of thick layers has been established, we proceed by including a plasma in the oxidation experiments. In Fig. 6.4, a plasma oxidation measurement at standard conditions of a sample identical to the one used in the previous section is shown. From Fig. 6.4, we conclude that a plasma increases the oxidation rate during oxidation and that larger oxide thicknesses can be obtained within reasonable times.

This can also be seen in Fig. 6.5 where the same data are plotted in correspondence with the inverse logarithmic law, similar as in Fig. 6.3. It is obvious that the effect of a plasma on the oxidation process cannot be explained by an increase of the temperature of the surface layers, since this would lead to a straight line with a slope and offset differing from the natural oxidation case. Gillies et al. [Gil00] performed plasma oxidation experiments in which the oxidation content were measured by Rutherford Backscattering Spectroscopy (RBS). The results are converted to oxide thicknesses\(^3\) and added to Fig. 6.5. Although the oxidation set-up and plasma conditions that were used are completely different and only a few data-points are available, it is clear that a behavior similar to our experiments is observed, indicating that plasma oxidation is universally deviating from the thermal oxidation process. In the next chapter we will go more deeply into the influence of the plasma by comparing dynamics measurements with plasma diagnostics.

\(^3\)For this calculation it is assumed that the layer is stoichiometric Al\(_2\)O\(_3\).
Figure 6.5: Ellipsometry during the natural oxidation (solid line) and plasma oxidation (dashed line) of Si / SiO$_x$ / Ta(3.5 nm) / Al(7.0 nm). The data are plotted semi-logarithmically as $1/l$ versus $(t + \tau)/l^2$. $\tau$ was taken to be 0.2 seconds. The data from Gillies were taken from [Gil00].

6.5 Plasma oxidation of thin aluminum layers on an insulating substrate

It was argued in section 3.2.6 that the oxidation dynamics can depend on the finite thickness of the aluminum layer. The interface between the aluminum and the substrate (or buffer layer) could influence the oxidation process in several ways:

1. The energy of bringing an Al ion into the oxide is influenced by the presence of Co atoms close to the Al/Co interface. It is not likely that more than one or two atomic layers close to the interface are affected significantly.

2. The chemical potential of electrons in the metallic aluminum is modified as the amount of aluminum that can provide electrons decreases.

3. The layer morphology (i.e. grains versus homogeneous structure) can have an influence on the oxidation process, and the morphology can depend on the layer thickness. See section 3.2.7.

Note that a thickness-dependent roughness of the deposited aluminum layer could also introduce a dependence of the oxidation rate on the Al thickness, but it is assumed that this effect is probably not significant. For complete
6.5. Plasma oxidation on an insulating substrate

tunnel junction structures, including a Ta buffer layer and Co bottom electrode, it has been shown by LeClair et al. that the roughness of the Co and Al layers is less than one monolayer [LeC02b].

In order to examine the influence of the interface, experiments were performed on samples with various thicknesses between 1 and 3 nm of aluminum. In order to maximize the effect of the interface, especially focussing on items 2 and 3 from the list above, SiO$_2$ is chosen as the substrate for its insulating properties. The sample structure is Si(001) / SiO$_2$(3 nm) / Al($x$). In Fig. 6.6 the raw, uncalibrated measurements are plotted. As has been mentioned in chapter 5, a direct quantitative calibration, converting ellipsometer signal to oxide thickness, is not possible since exact indices of refraction of the thin layers are not available. Indirectly, a calibration can be performed, as will be described here. It is observed that the 1.0 nm measurement shows no significant changes after about 1000 s of oxidation. It is assumed that the layer is completely oxidized at this point (since over-oxidation is not possible due to the SiO$_2$ underneath the Al), hence the amplitude of the ellipsometer signal at this point corresponds to 1.0 nm oxidation for this sample. For the samples with different Al-thickness, other calibration factors must be used (see section 5.3). These can be calculated using simulations, as in Fig. 6.7. The simulations show a sub-linear relation, i.e. the complete oxidation of a 3 nm Al layer would result in an ellipsometer signal that is only about 2.7 times larger than the complete oxidation of a 1 nm Al layer. Hence, the other measurements can be calibrated relative to the 1 nm measurement. The measurements are calibrated using these simulations and are shown in Fig. 6.8. In this figure, the 1 nm measurement is now correctly calibrated, but it may be obvious that the calibration can not be correct for the other three measurements: for example, the measurement of the oxidation of 3 nm of aluminum shows that after 1500 seconds almost 4 nm of Al has been oxidized, which is obviously not possible. We

![Figure 6.6: Raw measurements of the oxidation of Si / SiO$_2$ / Al($x$), with $x$=1.0, 1.5, 2.0 and 3.0 nm.](image)
suggest that this inconsistency is due to a small amount of oxide already present before the measurement starts and hence before the ellipsometer is set to zero. This \emph{initially oxidized Al} $d_{io}$ (in nm) is partially due to oxygen taken by the aluminum from the SiO$_2$, and partially due to oxygen from the background gas in both the sputter chamber and the oxidation chamber, before the measurement is started.

The small amount of “lost” aluminum influences the calibration procedure that was described above. Let us assume for example that 0.3 nm Al has already been oxidized. Effectively, this means that the measurement of the 1.5 nm sample should be calibrated using a simulation of the oxidation of only 1.2 nm Al, since the ellipsometer is only sensitive to changes in the amount of metallic material (the oxidized 0.3 nm Al is effectively “lost”). The 2.0 nm and 3.0 nm measurements should be calibrated correspondingly using 1.7 nm and 2.7 nm Al simulations, respectively. Mathematically,

$$d_{Al} = I_{ell} C (d_d - d_{io})$$  \hspace{1cm} (6.3)

where $I_{ell}$ is the ellipsometer signal, $C(x)$ is the calibration factor for a layer of $x$ nm (metallic) aluminum, $d_d$ is the amount of deposited Al. For various amounts of initially oxidized aluminum, $d_{io}$, the calibrated measurements are shown in Fig. 6.9. The assumption that 0.3 nm Al has been initially oxidized, in Fig. 6.9a, is apparently not enough to make the calibration consistent, and equally so for the 0.4 nm measurement (Fig. 6.9b). If it is assumed that 0.5 nm of Al is oxidized before the measurement, as depicted in Fig. 6.9c, the oxidation curves seem reasonable for each Al thickness: the 1 nm sample is oxidized completely, the 1.5 nm sample is almost completely oxidized, as are the 2 nm and 3 nm samples. It must be noted that the calibration depends sensitively on the exact amount of deposited Al, which could introduce larger errors. Angle resolved XPS may be used to determine more directly the exact amount of initial oxide.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6_7.png}
\caption{Simulations of the oxidation of Si / SiO$_2$ / Al($x$), with $x = 1.0$, 1.5, 2.0 and 3.0 nm. The simulations are rescaled such that the 1.0 nm simulation results in 1; of the other layers, 100% oxidation can now be determined relative to this.}
\end{figure}
6.5. Plasma oxidation on an insulating substrate

Figure 6.8: Measurements of the oxidation of Si / SiO$_2$ / Al($x$), with $x=1.0$, 1.5, 2.0 and 3.0 nm, calibrated using the assumption that the 1.0 nm measurement is completely oxidized after 1000 s. The vertical axis represents the amount of oxidized aluminum.

Figure 6.9: Measurements of the oxidation of Si/SiO$_2$/Al($x$), calibrated using various amounts of initially oxidized aluminum: a) 0.3 nm. b) 0.4 nm. c) 0.5 nm.

Now that we have calibrated the measurements, we analyze the oxidation rates in more detail in order to determine the effect of the interface as discussed at the beginning of this section. In Fig. 6.10 the oxidation rate (derivative with respect to time) is plotted versus the oxide thickness\(^4\). As a first observation, it is noted that for all oxide thicknesses the oxidation rate of a sample with a larger Al thickness is a lot higher than the oxidation rate of a sample with a small Al thickness. This is in sharp contrast with the

\(^4\)The amounts of oxidized aluminum are converted to oxide thicknesses by multiplication by 1.275, see appendix B.2.
growth laws from all models for natural oxidation of thick or semi-infinite layers (as reviewed in chapter 3), where the rate of oxidation depends only on the thickness of the oxide and the thickness of the remaining metal does not play a role.

For this apparent effect of the finite thickness of the aluminum several mechanisms were suggested in section 3.2.6 (and repeated at the beginning of this section, page 6.5). It is noted that the influence of the thickness of the deposited aluminum layer is very significant, when the oxidized thickness of Al is larger than about 1 nm. For the 2 nm and 3 nm cases, this means that the effect is significant already when there is still more than 1 nm and 2 nm Al remaining, respectively. Because of the long range over which the presence of the interface is “felt”, it is unlikely that the change in atomic bonding energy is responsible (option 1 mentioned on page 98). For the effect of the bottom layer on the work function an even shorter range was estimated in section 3.2.6 (option 2), hence we can neglect changes in work function and the corresponding change in the oxidation process.

The third option mentioned above is based on variations in the size of the metallic grains from which electrons tunnel towards the oxide surface; see also section 3.2.7. It was argued that the grain size might depend on the initial deposited thickness of the aluminum and that during oxidation the grain size decreases. It was derived that smaller grains will have a higher work function due to two effects: the dependence of the image-charge...
distribution on the grain radius and the positive charging of the grain due to the removal of electrons. The higher work function results in a lower voltage $V$ over the oxide, resulting in a lower oxidation rate. Qualitatively, the incorporation of this effect can explain the observed higher oxidation rate for thicker deposited Al layers. In order to make more quantitative statements it is necessary to obtain more information on the dependence of the grain-size and -shape on the deposited thickness and oxidation progress. Scanning Tunneling Microscopy (STM), Angle-Resolved XPS and especially (cross-section) Transmission Electron Microscopy ((X)TEM) and Spectroscopic Ellipsometry could give more information on the exact sizes and shapes of the grains.

### 6.6 Oxidation of sub-nanometer Al

As mentioned in the introductory and review chapters, sub-nanometer oxides are necessary for application in devices. For Al thicknesses below 1 nm the oxidation time must be extremely well controlled in order to prevent oxidation of the bottom electrode. In this section the oxidation dynamics and over-oxidation of 0.4 to 0.9 nm aluminum layers will be investigated.

Samples with a general structure of Si / SiO$_2$ / Ta(5 nm) / Co$_{90}$Fe$_{10}$ (5 nm) / Al($x$) were grown and oxidized under standard oxidation conditions. The raw ellipsometry measurements are shown in Fig. 6.11. Shown is the ellipsometer signal, which is linearly proportional (within 1%) to the amount of oxidized aluminum (verified by simulations, see section 5.3), as a function of time. An initial high rate of oxidation is observed, after which the oxidation slows down. After a short time, which is longer for thicker layers, the oxidation rate is increasing again. This is surprising, since until

![Figure 6.11](image-url)

**Figure 6.11:** Ellipsometry registration of the plasma oxidation of 0.4 to 0.7 nm Al on Ta(5 nm)/CoFe(5 nm).
now the rate of oxidation of a thick single layer of any material has been observed to decrease monotonously, see for example Fig. 6.6.

For the 0.5 nm measurement the 2nd derivative of the ellipsometer signal \( I \), \( \frac{d^2I}{dt^2} \), is slightly smoothed and plotted in Fig. 6.12 in order to more clearly observe the features (like increases, decreases) in the oxidation rate. Note that a positive second derivative implies an *increase* in the rate of oxidation, a negative second derivative implies a *decrease* in oxidation rate. Several important features in the oxidation rate are marked in the figure. The data for the other Al thicknesses show these features as well, although the times at which they occur vary. We conjecture that the following is happening:

**Region A and B.** During the first few seconds, the gas is let into the chamber and the plasma is ignited and becomes stable. The fluctuations of the oxidation rate probably correspond to the complex processes that happen within this start-up time, like initial thermal oxidation, plasma ignition and plasma stabilization\(^5\). Region B is longer for thicker deposited Al thickness, probably due to the same effect as in the measurements in the previous section: a thicker Al layer oxidizes faster (or holds a higher rate of oxidation for longer times)

**Region C.** The rate decreases again as the oxide grows thicker. We suggest that when, in this region C, the CoFe / Al - interface is reached, the thickness does not further increase much, but the O content does. This is consistent with the results by Kuiper *et al.* [Kui01a], who measured (see Fig. 6.13) a phase in which the oxide thickness is constant, but the oxygen content increases to stoichiometric \( \text{Al}_2\text{O}_3 \), before over-oxidation starts. This may imply that a minimum concentration of O at the CoFe/Al interface is

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\(^5\)See section 7.3.
necessary before the oxidation can proceed with the bottom electrode. Note
that the XPS-set-up of Kuiper is sensitive to these changes, but our ellip-
someter is not (see Fig. 5.5). The timescale of Kuipers experiments are
different from ours due to a different plasma and a larger layer thickness.

Region D. Over-oxidation, i.e. oxidation of the Co electrode, takes place
and the total oxide thickness increases.

Region E. In the last phase, the cobalt oxide becomes thicker and again
the rate of oxidation will decrease asymptotically to zero.

It must be noted that the RBS measurements of Kuiper et al. indicate that
the average stoichiometry of the complete oxide layer is Al$_2$O$_3$. However,
Koller et al. [Kol03] report an asymmetry in the height of the barrier. Al-
though the origin of this asymmetry is not clear, it is possible that the
concentration of O at the interface differs from the average. Therefore, for
over-oxidation to start, the stoichiometry of the oxide at the interface is not
necessarily exactly Al$_2$O$_3$. Furthermore, it must be noted that the process
prior to over-oxidation is unclear. Diffusion of O into the oxide, the most
obvious process of transport of O through the oxide, is not likely due to the
low rate of diffusion; see also section 3.2.3.

The assumption in this model that at the start of region D, at time $\tau_D$,
all aluminum is completely oxidized, can be used to calibrate the measure-
ments, since two points are known now: for the 0.5 nm measurement, for
example, at $t=0$, $d_{\text{ox}}=0$ and at $t = \tau_D$, $d_{\text{ox}} = 0.5$ nm, where $d_{\text{ox}}$ denotes the
amount of oxidized Al. However, as in the previous section, at time $t = 0$ a
small amount of initial oxide will be present: $d_{\text{ox}}(t = 0) = d_0$. Hence, the

![Figure 6.13: RBS (a) and XTEM measurements (b) dur-
ing the oxidation of 1.5 nm Al performed by Kuiper et al. [Kui01a]. The horizontal
dashed line in (a) indicates sto-
ichiometric Al$_2$O$_3$. The vertical
dashed line indicates that the oxidation continues approx-
imately at the point where the
Al$_2$O$_3$ is stoichiometric.](image-url)
calibration procedure is expressed as

\[ d_{\text{ox}}(t) = d_{\text{io}} + (d_{\text{d}} - d_{\text{io}}) \frac{I(t)}{I(\tau_D)} \]  

(6.4)

where \( d_{\text{d}} \) is the amount of deposited Al thickness, \( I(t) \) is the ellipsometer signal at time \( t \) and \( I(\tau_D) \) is the ellipsometer signal at \( t = \tau_D \), the point where over-oxidation starts.

This calibration is performed, initially without any initial oxide present \((d_{\text{io}} = 0)\) and the result is shown in Fig. 6.14. It will be shown that also in this case, an initial oxide is present before the measurement starts.

In order to verify the proposed model, XPS is used to determine the amount of over-oxidation by measuring the composition of identical samples after 3 s and after 9 s oxidation. Partial spectra of all samples around the Co-\(2p_{3/2}\) peak were measured. From Fig. 6.14, it is expected that the 3 s-XPS measurement only shows cobalt oxide in the 0.4 nm sample. The 9 s-XPS measurement should show cobalt oxide in all measurements. The 9 s oxidation measurements are shown in Fig. 6.15. The metallic and oxidic Co \(2p_{3/2}\) peak (778 eV and 780 eV, respectively) are clearly separately observed, as is a shake-up peak around 787 eV which is attributed to the oxide \(^6\) [Arm01] and should be included in the total oxide intensity. It was found that after 3 seconds plasma oxidation only the 0.4 nm sample was

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\(^6\)The shake-up peak is especially attributed to CoO, not to Co\(_3\)O\(_4\) since that oxide does never show a significant shake-up peak [Arm01].
6.6. Oxidation of sub-nanometer Al

Figure 6.15: XPS spectra of the samples after 9 seconds plasma oxidation.

slightly over-oxidized; in the thicker samples no clear CoO peak was observed. After 9 seconds oxidation some CoO was detected in all samples, including the 0.7 nm sample. This corresponds qualitatively very well to Fig. 6.14.

The absolute amount of Co-oxide can be determined from the ratio of the oxidic and metallic Co peaks in XPS, by the method described in section 4.4. We can now quantitatively verify the consistency of the proposed model by comparing the absolute amount of Co-oxide after 9 seconds oxidation, denoted by $d_{\text{xps}}(9s)$, with the change in the ellipsometer signal $\Delta I_{\text{Co}} = I(9s) - I(D)$. Theoretically, a linear relationship is expected between $\Delta I_{\text{Co}}$ and $d_{\text{xps}}(9s)$.

For each sample, the XPS data and the ellipsometry data are shown in Fig. 6.16a, and a curve is added to guide the eye. Apparently, no linear relationship is emerging. This probably results from some initial oxide that is present before the ellipsometry measurement starts, similar to the measurements in section 6.5. This implies that there is a smaller amount of aluminum which could be oxidized during the measurement. We can use $d_{\text{io}}$ as a fitting parameter: $d_{\text{io}}$ must be taken such that the values of $d_{\text{ox}}$ will display a linear correlation with the XPS data. It is found that if $d_{\text{io}} \approx 0.36$ nm a good linear agreement between XPS and ellipsometry data results (within the uncertainty of the measurements), as shown in Fig. 6.16b. The initial amount of oxide is smaller than the 0.5 nm found in the previous section. This is probably due to the fact that in those experiments the aluminum was deposited directly on SiO$_2$, which causes some Al$_2$O$_3$ to be created by aluminum stealing oxygen from the SiO$_2$. The uncertainty in the ellipsometry data shown in the figure results partly from small deviations in deposited Al thickness. A larger source of uncertainty is probably created by small differ-
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Figure 6.16: Co-oxide thickness, as measured by XPS after 9 seconds plasma oxidation, versus the change in the ellipsometer signal after the Co-oxidation starts. In a) no initial oxide is taken into account. In b) the initial oxide is 0.36 nm.

ences in the amount of initial oxide due to variations in duration of transport to the oxidation chamber. Finally, in the calculations it is assumed that all layers are homogeneous and perfectly flat, which is probably not correct due to, for instance, the grain-like structure of the layers. The amount of CoO calculated from the XPS experiments depends on the exact distribution of the CoO and Co underneath the aluminum oxide, hence some uncertainty is introduced.

In Fig. 6.17 the measurements are shown again, calibrated according to the model discussed above, including 0.36 nm of initial oxide. The horizontal dashed lines indicate 100% aluminum oxidation (the point at which over-oxidation starts) based on the proposed model. For each measurement the onset of over-oxidation of the CoFe bottom electrode is indicated by a small vertical line. The dashed vertical lines indicate the times when the two separate XPS measurements were preformed. The scales are identical for each measurement in the graph, and it can be clearly observed that indeed the samples with thinner Al top layers over-oxidize faster. A more direct quantification of the amount of over-oxidation using the ellipsometer cannot easily be made due to unknown optical constants of the layers, which probably depend on the growth conditions. It is concluded that in specific conditions (e.g., for sub-nm layers\footnote{For thicker layers, the rate at $t = \tau_D$ is low, such that features are obscured by noise and random fluctuations in the measurement.}), \textit{in-situ}, real-time differential ellipsometry can potentially be applied for \textit{in-situ} oxidation control, by stopping the oxidation process as soon as region D is reached.
6.7. Further research topics

In the remainder of this chapter, we investigate more complex structures and oxidation “schemes”, which again illustrate the power of the in-situ ellipsometer set-up. As this represents a preliminary study of potentially future research directions, the results will be discussed only qualitatively.

**Influence of the buffer layer**

As has been mentioned before, the buffer layers can induce a different growth of the aluminum layer, which can have an influence on the oxidation dynamics. A series of experiments was performed in which the top layer was kept the same: 2 nm of aluminum. The buffer layers were varied in order to induce different growth modes of the aluminum layer. In Fig. 6.18 the measurements are shown. The series is started with a standard stack consisting of a tantalum buffer layer and a cobalt bottom electrode (a). A standard
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Figure 6.18: A series of measurements in which the top layer was 2 nm of aluminum, with various buffer layers.

oxidation curve is observed, comparable to Fig. 5.8. Next, a sample is grown without Co (the aluminum is deposited directly on the Ta buffer) and oxidized. The signal is somewhat lower, which cannot be due to the decrease in metallic material\(^8\). Furthermore, the oxidation seems to slow down faster than the previous measurement. In measurement (c), a much thinner Ta buffer layer is used. It is obvious that the measurement displays completely different oxidation dynamics: first the ellipsometer signal decreases, and increases again after a short time. This behavior can only be simulated if the index of refraction of the aluminum layer is made dependent on the aluminum thickness and structure. It is known that the index of refraction of a layer with a high roughness or a grain-like structure can be completely different from the bulk value, and this index of refraction will depend on the size of the grains or the amount of roughness [Azz77]. With a fictitious grain-like structure, a roughly similar behavior of the oxidation dynamics was simulated (not shown). We suggest, therefore, that the small thickness of the Ta buffer layer induces an aluminum layer with a much larger roughness, as opposed to the thicker buffer layer that is normally used for magnetic tunnel junction structures.

In a different series of experiments ruthenium (Ru) was used as the buffer layer. As a function of Ru thickness, the measurements are shown in Fig. 6.19. A gradual change in shape of the curve as a function of Ru thickness is observed. We suggest that this is due to a gradual change of

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\(^8\)In section 5.3, page 85, it was remarked that less metal should result in a larger signal.
6.7. Further research topics

Figure 6.19: A series of measurements on Si / SiO_x / Ru(x) / Co (1.0 nm) / Al (1.0 nm), where the buffer layer thickness was varied between 0.7 and 2.5 nm. Soon after the start of the plasma, an anomaly is observed, of which the exact form depends on the buffer layer thickness. Measurements are shifted for reasons of clarity.

growth mode induced by the Ru thickness.

For a better qualitative and possibly quantitative interpretation more information on the exact evolution of the structure during the oxidation process is needed, as is the dependence of the structure of the aluminum as a function of buffer composition. This can be done by using STM and AFM, and in-situ spectroscopic ellipsometry during the oxidation process.

The obvious dependence of the shape of the oxidation curve on the morphology of the top layer can potentially be used as a fast (but destructive) characterization tool: in a series of oxidation experiments in which the composition of the buffer layer is varied, the oxidation curve can indicate when the growth of the aluminum changes from flat to strongly granular.

Influence of a thermal oxide

Two experiments were performed in which the aluminum layer was first oxidized thermally in standard conditions (10 Pa, room temperature) for a certain time before the plasma was ignited. These measurements are shown in Fig. 6.20 and compared with a standard measurement in which the plasma is turned on immediately. In this figure, it is observed that after approximately 17 minutes of (total) oxidation time (indicated in Fig. 6.20 by the dashed line), the three curves practically overlap, implying that at that time the same amount of Al has been oxidized. At the same point, it can be observed that the fully plasma-oxidized sample has a somewhat higher rate of oxidation as compared to the two thermally oxidized samples. Since the oxide thickness and the plasma conditions are the same, this suggests that the oxide formed by thermal oxidation has properties (barrier height, oxide voltage, impurities, thickness homogeneity, etc.) that are different from the fully plasma-oxidized oxide. It must be noted, however, that the difference is very small and almost within the uncertainty of the measurements and that
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Figure 6.20: A series of measurements on Si / SiOx / Ta(3.5 nm) / Co (4.0 nm) / Al(2.0 nm). In measurement a) the plasma is ignited immediately when the oxygen is let into the chamber. Measurement b) and c) are oxidized thermally for 100 s and 300 s, respectively, before the plasma is ignited. The vertical dashed line indicates the time at which the oxide thicknesses are the same, but the individual rates are not.

this effect has been found difficult to reproduce. In view of the discussion on the difference in the $R \times A$ product and TMR between thermally and plasma-oxidized magnetic tunnel junctions (see section 1.3, especially Fig. 1.5), it is certainly interesting for further investigations.

6.8 Conclusions

In this chapter, we have used the in-situ ellipsometry technique for oxidation dynamics studies. Using this technique, a value for the sticking coefficient was determined for poly-crystalline Al layers. Furthermore, the correct model for the natural oxidation process was determined to be the model by Cabrera that results in the inverse logarithmic law. The limiting step in this model is the solution of aluminum ions into the oxide, assisted by the field over the oxide, which is dependent on the thickness of the oxide.

Additionally, it has been found that plasma oxidation cannot be explained straightforwardly in terms of the inverse logarithmic model as a simple increase of the temperature of the surface layers. Plasma oxidation experiments of Al-layers of various thicknesses on SiO$_2$ showed an influence on the rate of oxidation at practically all oxide thicknesses. It was con-
cluded that the influence of the thickness of the aluminum layer stems from the dependence of the grain-size and -shape. Unfortunately, due to the large number of unknown variables it is not possible to quantify this. STM, AFM, Angle-Resolved XPS and spectroscopic ellipsometry could give information with which a model can be formulated for the behavior of the sizes and shapes of the grains as a function of the deposited Al thickness and oxidized fraction.

In experiments on oxidation of ultra-thin layers on (ferromagnetic) metallic underlayers, aimed at low-resistance applications of magnetic tunnel junctions, it was found that under certain circumstances over-oxidation can be observed directly using the ellipsometer. This is potentially applicable as process control in industrial production lines for determining the optimum oxidation time and conditions for magnetic tunnel junctions.

Additionally, in experiments with various compositions of the buffer layer, it is found that the morphology of the aluminum depends sensitively on the buffer layer and bottom electrode, and has a strong effect on the oxidation process and ellipsometry results. Unfortunately, more quantitative results can only be obtained when more knowledge of the morphology is made available using e.g., STM, AFM or spectroscopic ellipsometry.
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Chapter 7

Dynamics of the Plasma Oxidation Process

7.1 Introduction

In this chapter we examine the influence of the plasma on the oxidation process, by combining measurements on the oxidation dynamics in various plasma conditions with measurements on the properties of the plasma. For the oxidation dynamics we again use the in-situ ellipsometer described in chapters 5 and 6. For the characterization of the plasma we use a variety of techniques: Langmuir probes, Two-photon Absorption Laser Induced Fluorescence (TALIF), Optical Emission Spectroscopy (OES) and Actinometry. The results will be given in the following sections and only shortly discussed individually since an in-depth analysis of the plasma is far too complicated for the purpose of this work. The collection of all results will be summarized and extensively discussed, leading to a novel model for the plasma oxidation process of aluminum. With this model the oxidation rate as a function of plasma parameters can be predicted, including the dependence on the oxide thickness. Using this model, we give some suggestions to explain the influence of the plasma oxidation process on the properties of a magnetic tunnel junction.

7.2 The oxidation rate in various plasma conditions

The in-situ analysis allows monitoring of the oxidation dynamics during the oxidation process. The samples used in this chapter are 2.0 nm aluminum on Si / SiOx / Ta(3.5 nm) / CoFe(4.0 nm) to ensure that the structure of the aluminum is comparable to actual tunnel junctions. At various plasma pressures, oxidation experiments were performed over a range of plasma
currents. It has to be taken into account that, at a certain plasma current, the power depends on the pressure, as shown in Fig. 7.1.

Figure 7.2 displays the ellipsometry measurements of the oxidation process of the standard samples in a standard pressure plasma (10 Pa) at various plasma currents and corresponding plasma powers. A calibration is done using the earlier results of LeClair [LeC02b], who found that in 200 seconds the thickness of 2.0 nm is optimally oxidized, i.e. no over-oxidation has taken place. In our measurements, after about 200 seconds the oxidation has slowed down considerably. Therefore, it is assumed that the oxidation of Al is practically complete at approximately this point. This is a crude calibration which introduces an uncertainty in the oxidized thickness of about 5%. As the oxide thickness increases, fluctuations in the signal and small differences (in deposited thickness, alignment) between measurements become dominant. Differences in the rate of oxidation can be best observed when the oxidation rate is high, corresponding to small oxide thicknesses,
below 1.5 nm. In Fig. 7.3 the oxidation rate (i.e. the slope in Fig. 7.2) is plotted versus the amount of oxidized aluminum. A high oxidation rate is observed for small oxide thicknesses, decreasing rapidly. Around 0.5-0.7 nm a transition to another regime seems to appear, which will be discussed in section 7.8. After this transition region, the rate decreases more slowly. In order to investigate the oxidation rate in various plasma conditions, we will use the oxidation rate at an (arbitrary) oxide thickness of 1 nm, as indicated by a vertical line in figure 7.3. The uncertainty introduced is estimated to be about 15%, due to small variations in deposited Al thickness, sample alignment in the ellipsometer (oxidation chamber), and initial oxide (due to variations in transportation time).

In Fig. 7.4 the oxidation rate at a fixed oxidized thickness of 1 nm Al as a function of plasma power and pressure is represented. Least-square fits for each pressure reveal a linear dependence on the plasma power. The linear correlation with the plasma power is observed for all oxidized Al thicknesses between 0.6 nm and 1.5 nm as well; outside this region the determination of the rate is less reliable. In contrast to these results, in measurements (using...
Chapter 7. Dynamics of the Plasma Oxidation Process

RBS, similar to Fig. 6.13) by Kuiper et al., a decrease of the oxidation rate with increasing pressure is observed [Kui01a]. Apparently, the plasma used in their set-up displays oxidizing properties that are different from ours, making a direct comparison difficult.

It is observed in Fig. 7.4 that the oxidation rate extrapolated to zero plasma power is not zero. Such an “offset” is observed for all thicknesses. This might be indicative of a power-independent component of the plasma oxidation process. Possibly this observation is related to thermal oxidation parallel to the plasma oxidation process. However, in a comparison with the thermal oxidation measurement in section 6.3 it is found that (at 1 nm oxidized thickness) the rate of thermal oxidation is much lower (by 3 to 5 orders of magnitude) than the oxidation rates at zero plasma power. The observed power-independent component of the plasma oxidation rate can therefore not be explained by thermal oxidation parallel to plasma oxidation. The power-independent component could possibly be caused by a species or process in the plasma that is saturated at very low plasma powers.

More insight in the oxidation process can possibly be obtained from varying the distance from the plasma source to the substrate. The resulting oxidation rates at an oxidized thickness of 1.0 nm as a function of the distance between the plasma source and the sample are shown in Fig. 7.5. As the distance is increased, a decrease in oxidation rate is observed.

![Figure 7.5: Oxidation rate vs. the separation between the plasma source and the substrate. The center measurement was made at the standard distance of 37 mm.](image)

We performed an experiment to examine how long the oxidation proceeds when the plasma is turned off. In this experiment, the plasma power source is turned off for several short periods, shown in Fig. 7.6. It is observed that, as soon as the plasma power source is turned off, the oxidation process stops practically immediately, within less than two seconds. This suggests that the particle or particles from the plasma responsible for the oxidation process have a short lifetime, or lose their energy very fast (via collisions) after the power is turned off.
7.3 Ignition behavior and stability of the plasma

In order to be able to compare the measurements on plasma properties in this chapter with actual oxidation processes, it is important to have knowledge about the ignition process and stability of the plasma. It is essential that the plasma does not change significantly during the oxidation process.

It is observed by eye that the plasma ignites practically immediately after the gas is let into the chamber. During the oxidation process the plasma voltage changes slowly (at a time scale of minutes) by about 5%, and the pressure decreases by a few percent as well\(^1\).

In order to quantify the observations, the ignition behavior and stability of the plasma under standard conditions \((I_{\text{plasma}} = 7.5 \text{ mA}, P \approx 6 \text{ W}, p = 10 \text{ Pa})\) have been measured using double Langmuir-probes and emission spectroscopy. A fixed bias voltage (10 V) is applied between the probes\(^2\) and the current (mostly ions) through the probes is recorded during the start of the plasma and during the first hundreds of seconds. This is shown in Fig. 7.7a. As indicated by the Langmuir probes, within approximately 1.5 seconds after ignition the ion current is practically stable\(^3\). The spectroscopic measurement, Fig. 7.7b, where the intensities of two oxygen lines

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\(^1\)Recall that the power supply is current-limited; a change in pressure will therefore cause a change in electrode voltage and a slight variation in the power, see Fig. 7.1.

\(^2\)It was earlier verified that the current through the probes is not a significant part of the plasma current, i.e. less than 1% of 7.5 mA.

\(^3\)The probe set-up averages in about 50 ms, hence no significant delay is expected.
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Figure 7.7: During the start of a standard plasma, the Langmuir probe current (b) as well as the areas of the 777 nm (O(5P)) and 845 nm (O(3P)) peaks using the spectrometer were recorded. The inset in (a) shows a close-up of the behavior at longer time scales.

have been followed, shows a slower start-up behavior ($\approx 4 \text{ s}$), partially due to the 2-seconds averaging of the spectrometer and partially due to the slower chemical processes in the plasma.

Note that for the sub-nm Al layers from the previous chapter, for which typical oxidation times are less than 10 seconds, the start-up time of the plasma and small variations in it can well be of importance. It can therefore not be assumed that in this case the plasma is constant throughout the oxidation process, which is important for the optimization of the oxidation time.

The inset in Fig. 7.7a shows the variation in probe current at longer timescales. A slow fluctuation of a few percent is observed. The observed fluctuations are probably due to a small increase in the temperature of the gas and the electrodes, and possibly to slow changes in the composition of the gas. As has already been noted, the pressure of the gas is observed to decrease during the plasma run, by about 2% in 200 seconds and 5% in 30 to 60 minutes. This pressure drop can be caused by the absorption of oxygen on the reactor walls and the sample and, as we will see further on, the formation of ozone (see section 7.6, p.131). Additionally, the readout of the Pirani pressure gauge is dependent on the gas temperature and composition$^4$.

We conclude that a measurement of a plasma characteristic taken after some time is within 5% representative for the total oxidation time after an initial 1.5 seconds after ignition.

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$^4$A Pirani pressure gauge measures the cooling rate of a hot wire, which is a measure of the gas pressure but depends of course on the gas temperature and the mass of the molecules or atom as well. The actual gas temperature has not been measured.
7.4. Electron temperature and ion density

Power is coupled into the plasma via electrons by an external electric field. The electrons then can transfer their energy by elastic and inelastic collisions to the background gas; heating the gas, exciting other atoms or ionizing other particles. As explained in chapter 3, charged particles, i.e. electrons and ions, could play a role in the oxidation process in various ways. Furthermore, information on the electron temperature is necessary in the determination of the O density by actinometry (section 7.6). Therefore, the properties of electrons and ions in the plasma under investigation must certainly be examined. Using the Langmuir probe technique, described in section 4.8, the electron temperature $T_e$ (eV) and the positive ion density $n_+$ (m$^{-3}$) can be determined as a function of the plasma parameters mentioned in the previous section.

A series of experiments was performed as a function of power, shown in Fig. 7.8. The ion density increases practically linear with the power over a large range of powers, which is encountered in most plasmas (see [Lie94]). The electron temperature $T_e$ increases from 1.5 eV and saturates at a constant value of approximately 2.0 eV for powers above 2 W.

Next, the plasma pressure was varied while keeping the power constant; the resulting electron temperature and ion density are shown in Fig. 7.9. The electron temperature decreases slightly. The strong decrease of the ion
density as a function of pressure is not normally encountered in plasmas. It is tentatively explained by more elastic and inelastic collisions of electrons with O$_2$, which results in less energy to ionize molecules. This is due to two effects: diffusion of ions towards the sample position is slower and the ionization is lower due to the decrease in the electron temperature. However, for a more thorough explanation a sophisticated and complete model of the plasma needs to be developed, which is beyond the scope of this thesis.

Finally, the dependence on the separation between the plasma source and the sample was measured and is shown in Fig. 7.10. Standard power (6 W) and pressure (10 Pa) were used. Note that, as with the ellipsometry measurements, the separation could not be varied over a large range. The ion density decreases over this range, which is due to the approximate spherical diffusion in all directions, assuming that the rate of e + O$_2$ recombination in the gas phase is negligible compared to diffusion. The electron temperature appears to remain constant, which is unexpected. This observation is possibly due to the dependence of the collision cross-section of electrons on the energy. As the Langmuir-probe technique mostly detects electrons in the higher-energy tail of the energy distribution, an incorrect picture of the electron temperature can be created due to larger collision-cross-sections for electrons with a lower energy [Lie94].

The Debye length, the characteristic length-scale of disturbances and sheaths in a plasma (section 3.3.2), can now be determined as a function of
the plasma parameters as well:

\[
\lambda_D = \sqrt{\frac{\epsilon_0 \hat{T}_e}{en_e}}. \tag{7.1}
\]

As the electron temperature is practically constant for all plasma parameters, \(\lambda_D\) depends solely on the inverse of the square root of the ion density in the plasma. The Debye length is shown for all plasma parameters in Fig. 7.11. The Debye length will be used to determine the charge density at the surface in section 7.7.

Summarizing, we have found that the ion density increases almost linearly with the plasma power, and decreases as the pressure is increased or the distance to the plasma source is increased. The electron temperature varies only slightly around 2 eV.

### 7.5 Detection of atomic oxygen and ozone using TALIF

In order to obtain information on the density of both atomic oxygen and ozone, two-photon absorption laser induced fluorescence (TALIF) measurements were performed\(^5\). The technique and experimental apparatus have been described in section 4.9.

\(^5\)The TALIF experiments have been published in [Kne04].
First, it was verified that the laser does not dissociate oxygen molecules by measurements done with and without a plasma, both before and after a plasma was ignited. It was observed that the TALIF-signal requires about 20 minutes before the steady state level is reached, indicating that the chemistry of the production of the O and/or O$_3$ is a slow process. In Fig. 7.12 measurements are shown performed before a plasma was run, with only oxygen in the chamber (a), in a plasma (b), and approximately 30 minutes (c), and 60 minutes (d) after the plasma is turned off but with the gas still in the chamber. From Fig. 7.12a we conclude that the laser does not significantly dissociate oxygen. The cross-section for dissociation by photons of 5.5 eV is much higher for ozone ($\sigma_{O_3}^{d} = 3.23 \times 10^{-18} \text{cm}^2$) than for O$_2$ ($\sigma_{O_2}^{d} = 3.21 \times 10^{-24} \text{cm}^2$), explaining the fact that we do not see any signal if only pure O$_2$ is present in the chamber. In Figs. 7.12c and d, still a large peak of practically the same shape is measured, from which we conclude that the TALIF-detected particle in our chamber has a very long lifetime - the decay time is of the order of hours. This points to ozone, which is a stable particle. The long lifetime is compatible with the observations of Zhukov et al. [Zhu00], who find that in their set-up the decay time of ozone is of the order of a few hours. Furthermore, dissociation of ozone was found to be the greatest on “pure” metallic surfaces, like the capacitance manometer used in their set-up. In the oxidation chamber used here, the surfaces will consist of oxide (and are probably saturated with oxygen), resulting in a low rate

![Graph](image)

**Figure 7.11:** The Debye length as a function of power (a), pressure (b) and distance (c), determined from the Langmuir probe results in Figs. 7.8 to 7.10.
7.5. Detection of atomic oxygen and ozone using TALIF

Figure 7.12: TALIF, with and without plasma. a: pure oxygen. b: during a plasma. c: 30 minutes after the plasma is turned off. d: 60 minutes after the plasma is turned off.

of ozone dissociation and therefore long lifetime of the ozone.

The peaks in Fig. 7.12b, c and d show that only one species is contributing to the TALIF peak, of which the temperature (derived from Doppler broadening) is about 10000 K or ≈ 1 eV (Eq. 4.10). Furthermore, the fact that the measured particle has such a long lifetime indicates again that it is ozone that is measured - the lifetime of atomic O is expected to be much shorter than that due to fast recombinations at walls. We conclude that only ozone is detected and that the density of atomic oxygen in the ground state is too low with respect to the O$_3$ density to be detected in our measurement. In the following experiments the peak is fitted with a single Gaussian of which the area, the total fluorescence intensity, is proportional to the ozone density.

We note that the detection of O created from ozone occurs during the same laser pulse in which the molecule was dissociated, because between two laser pulses (0.05 s), enough collisions to thermalize the hot atom to the background gas temperature would have happened (typical collision time of O is $10^{-5}$ s, about 5000 collisions between laser pulses).

The minimal amount of ozone that is present in the chamber can be determined: assume that the signal of O from O$_2$ in Fig. 7.12a is just disappearing in the noise (i.e. less than ≈ 2% of the O$_3$ signal):

$$\frac{I_{O_2}}{I_{O_3}} = 0.02,$$

where

$$I_{O_2} = P \sigma_d^{O_2} [O_2] \quad \text{and} \quad I_{O_3} = P \sigma_d^{O_3} [O_3],$$

(7.2)
where $P_l$ is the laser intensity, and $[X]$ denotes the density of a particle. Using the ratios of the intensities and the known density of O$_2$ ($2.4 \times 10^{21}$ m$^{-3}$ at 10 Pa), we find that the minimum density of ozone is $10^{18}$ m$^{-3}$. In the next section we give an estimate of the absolute amount of ozone present in the chamber.

The following measurements are performed while the plasma is on. In between measurements the chamber was pumped down and refilled with oxygen in order remove the long-living ozone from the previous measurement.

Next, we varied the plasma power around the standard value of 6 W. The results are shown in Fig. 7.13. The increase in power causes the intensity to increase, which indicates an increase in the density of the ozone in the plasma. This might be due to a higher production rate if more dissociations of O$_2$ and subsequent recombinations of O$_2$ + O take place. Remarkably, the width of the peak decreases, implying an unexpected decrease of the temperature of the measured atoms. In Fig. 7.14 the plasma pressure was varied while keeping the power constant at 6 W. With increasing pressure, both intensity and width decrease. TALIF measurements at several positions between the sample and the plasma electrodes were performed as well, but it was found that the signal is constant throughout the oxidation chamber, at least between the sample and the electrodes. This implies that the ozone density is practically uniform in the chamber. The dependence of the TALIF intensity on plasma power and pressure can be accounted for by variations in the density of ozone. The change in “temperature”, however, cannot be explained by variations in temperature of the ozone because they are probably smaller than the change of 5000 K that is observed. Neither can

![Figure 7.13: Variation of the plasma power; the pressure was 10 Pa.](image)

- ■: Intensity; ▲: Width of the peak, converted to the corresponding temperature (K).
the observed behavior of the temperature be due to collisions of the O-atom between dissociation and excitation, since during one laser pulse of 8 ns not many collisions occur (typical collision time of O is \(10^{-5}\) seconds). Therefore, only the internal energy of the ozone in the form of excited states can be of influence:

\[
E_O \leq h\nu - E_{b,g} - E_i,
\]

where \(E_O\) is the kinetic energy of the oxygen atom, \(E_{b,g}\) is the binding energy of the ground state, and \(E_i\) is the internal energy of the ozone molecule. The internal energy can be dependent on the plasma conditions. The decrease of the temperature as the pressure is increased is easily explained by an increased amount of quenching collisions of excited ozone. The decrease of the apparent “temperature” as the plasma power is increased, can be tentatively explained by an increase in the number of super-elastic collisions with electrons:

\[
e + O_3^* \rightarrow e + O_3,
\]

in which the electron can increase its kinetic energy by taking internal energy from the ozone molecule.

In conclusion, the TALIF measurements revealed that ozone is present more abundantly than atomic oxygen - the atomic O density could not be determined using TALIF. The ozone present in the chamber has a very long lifetime of the order of hours and a considerable amount of ozone remains therefore in the chamber after the plasma power has been turned off. Next, we will measure the atomic oxygen density using actinometry.

**Figure 7.14:** Variation of the plasma pressure; the power was kept constant at 6 W. ■: Intensity (arb.u.). ▲: Width of the peak, converted to the corresponding temperature (K).
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7.6 Detection of atomic oxygen using actinometry

As mentioned before, one of the most characteristic features of practically all plasmas is the emitted light. The emission of light enables identification of the particles that are present in the plasma. In certain cases, more information can be extracted, like density and temperature of those particles.

The optical emission spectroscopy (OES) technique is the most simple and non-intrusive method for examining a plasma. A spectrograph is all that is needed to record spectra and databases are used to identify peaks in the spectrum. This technique has been used by Kuiper *et al.* [Kui01a], in order to detect reactive species such as O radicals and molecular oxygen ions. The densities of O($^5P$) and O$_2^+$ were determined by taking the maximum peak intensity of the O($^5P$) 777 nm line and the 555 nm line of O$_2^+$. It will be shown in this section that this is an oversimplification. Kuiper *et al.* find an increase in O($^5P$) density relative to the O$_2^+$ density when the pressure is increased. As mentioned in section 7.2, their oxidation dynamics measurements show a decrease in oxidation rate when the pressure is increased, in contrast to the measured increase of the O($^5P$) atom density.

By assuming that the higher pressure causes more collisions to occur before the atoms reach the sample, thereby decreasing the thermal energy of the atoms, they conclude that probably thermalized excited O atoms are the main contributor to the fast plasma oxidation process.

Returning to the plasma under investigation, a spectrum of the plasma used in our set-up in standard conditions (10 Pa, 6 W) is shown in Fig. 7.15. From the peaks we find that the following particles are present: O in various excited states, O$^+$ and O$_2^+$. We will focus on the density of atomic oxygen in the discharge, therefore we apply the measurement scheme outlined in section 4.10: we add a small amount of argon and concentrate on the argon peak at 750 nm and two peaks of atomic oxygen at 777 nm and 845 nm. An amount of 4% O$_2$ was replaced by Ar in order to maintain the same pressure. It was verified that the addition of this amount of Ar does not significantly influence the plasma (as observed in the oxygen spectrum), especially only minor effects on the 777 nm and 845 nm peaks were observed. A partial spectrum of a typical plasma to which argon is added is shown in Fig. 7.16.
Figure 7.15: Spectrum of the plasma in standard conditions (10 Pa and 6 W). The peaks that were identified are labelled.
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Figure 7.16: Spectrum of the plasma in standard conditions (10 Pa and 6 W) to which 4% Ar was added. The oxygen and argon peaks that are used for actinometry are indicated. For the determination of the peak area, a simple horizontal background is subtracted.

As a first remark, it is noted that in all experiments, the oxygen 777 nm peak is about 10 times larger (in area) than the oxygen 845 nm peak. This is unexpected according to calculations using the reaction rates determined in section 4.10, which show that the 845 nm peak should be larger relative to the 777 nm peak. We suggest that the upper level, O(\(^5\)P), of the 777 nm line has one or more extra production channels. Several channels are possible. For instance, via cascading de-excitation from higher levels the two upper levels can be extra populated, resulting in extra emission. In order to determine whether the 3p(\(^5\)P) level is preferred with respect to the 3p(\(^3\)P) level, a highly sophisticated model of this specific oxygen plasma is necessary. An additional channel (see Fig. 7.17) that populates the 3p(\(^5\)P) and 3p(\(^3\)P) levels is electron excitation from the corresponding lower level\(^6\). The

\[
\begin{align*}
&\text{2p}^23s^2\text{ }^3S \\
&\text{2p}^23p\text{ }^5P \\
&\text{2p}^23p\text{ }^3P \\
&\text{1015} \ (2.10^3) \\
&\text{845} \ (3.10^3) \\
&\text{672} \ (1.10^3) \\
&\text{777} \ (4.10^3) \\
&\text{2p}^23s\text{ }^5S \\
&\text{2p}^23s\text{ }^3S \text{ Metastable} \\
&\text{2p}^23p\text{ }^3P \\
&\text{2p}^23p\text{ }^5P \\
\end{align*}
\]

\footnote{\text{We assume that the cross-section of electron excitation of the “crossed” transition, }\(^5\)S\rightarrow^3\text{P}, \text{ is lower than the transition }^5\text{S}\rightarrow^3\text{P} \text{ because a lower Einstein coefficient }A \text{ (as shown in Fig. 7.17) in generally accompanies a lower cross-section of electron excitation of that transition, see [Lie94], page 72, 73. Therefore, electron excitation to the }^3\text{P} \text{ level from the }^5\text{S} \text{ level is unlikely.}}}

Figure 7.17: Close up of the four oxygen levels that are used for actinometry. The arrows indicate radiative de-excitation, the numbers attached are wavelengths (nm) and in brackets the corresponding Einstein coefficients (s\(^{-1}\)) are shown. The 3s\(^5\)S level is metastable.
metastable $3s(^5S)$ level, which has a much longer lifetime than the lower level $3s(^3S)$ of the 845 nm line, is therefore available for extra electron excitation to the $^5P$ level, resulting in a higher 777 nm emission. These extra channels make the 777 nm line unsuitable for actinometry on this plasma. Therefore, we will focus on the 845 nm line of oxygen only. It must be noted that in the 845 nm line such an extra parasitic emission might occur as well, resulting in estimations of the oxygen density that are possibly too high. The exact influence can only be determined by advanced modelling of all plasma processes.

Similar to the oxidation dynamics experiments, the spectra of the plasma close to the sample surface (approximately 10 mm) were recorded at a range of plasma powers in various gas pressures. Using the theory outlined in section 4.10 we calculate the O density, which is shown in Fig. 7.18. It is observed that, as the power is increased, the O density increases rapidly from zero to a practically constant value; above about 4 W the density is independent of the power and increases with increasing gas pressure.

The degree of dissociation, $[O]/[O_2]$, increases from zero to roughly 1.3% for all pressures. Using these values, we can make an estimate of the ozone density; of which only a minimal value was calculated in section 7.5: $10^{18}$ m$^{-3}$. The TALIF-measurements displayed some noise, hence we can assume that the O-signal just disappeared in the noise on a TALIF peak. The O-signal would then be less than 10% of the ozone signal. It is safe to assume that the dissociation of $O_3$ is very fast compared to the TALIF process, which implies that TALIF has an identical sensitivity to ozone and atomic oxygen. Under these assumptions, the ozone density is therefore approximately 10 times higher than the O density. This means that about 10% of the oxygen is converted to ozone. This “conversion” of $O_2$ to $O_3$ can very well explain the observed pressure decrease of 5% (section 7.3) and the long timescale of the pressure decrease is in agreement with the observation

---

$^{7}$The oxygen density, $[O_2]$, is calculated via $n = p/k_BT$. 

---

Figure 7.18: Actinometry: ground state O density directly above the sample position as a function of plasma power, at various pressures.
that the ozone chemistry is a slow process, cf. section 7.5.

An actinometry spectrum was recorded at several positions between the sample and the plasma electrodes, as shown in Fig. 7.19. It is observed that the O density closer to the sample is lower than the density closer to the plasma electrodes. Note that, different from the TALIF and Langmuir probe measurements, the plasma electrodes are now at a constant distance and only the measurement position is varied. It is reasonable to assume that a similar behavior is observed when the plasma electrodes are moved: if the separation between sample and plasma is increased, the O density decreases.

![Figure 7.19: Actinometry: ground state O atom density in standard conditions ($p = 10$ Pa and $P \approx 6$ W) measured at several positions between the sample and the plasma source. The curved line is added as a guide to the eye.](image)

In conclusion, we have found that atomic oxygen is present abundantly in the plasma; the degree of dissociation is of the order of 1% for all plasma conditions. The O density $n_O$ increases with increasing plasma pressure, but depends only very weakly on the plasma power. Using the absolute values of the O density, an estimate has been calculated for the ozone density: about 10% of the O$_2$ density.
7.7 Overview and discussion

In Fig. 7.20, all results obtained in previous sections are shown schematically in order to be able to compare them qualitatively. As a function of the three plasma-parameters power, pressure and distance between sample and plasma, the behavior is shown of all quantities measured in the previous sections: ion density $n_+$, ozone density $n_{\text{O}_3}$, O density $n_{\text{O}}$, oxygen density $n_{\text{O}_2}$, electron temperature $T_e$, Debye length $\lambda_D$, and the surface charge due to the plasma $\sigma_s$, and finally the oxidation rate $R_{\text{ox}}$. If there is a single particle in the plasma responsible for the high rate in the plasma oxidation process, the oxidation rate can be expected to depend on the flux towards the sample (proportional to the density of that particle close to the sample). However, in the figure, no clear correlation between the oxidation rate and the density in the plasma of any particle is found.

Additionally, it was observed that plasma oxidation stops practically immediately as soon as the plasma power is turned off (Fig. 7.6). Since ozone was detected in great abundances after the plasma was turned off.

![Figure 7.20: Schematic overview of the dependence on the plasma parameters pressure, power and distance (of which the range is indicated) of the ion density $n_+$, ozone density $n_{\text{O}_3}$, O density $n_{\text{O}}$, oxygen density $n_{\text{O}_2}$, electron temperature $T_e$, Debye length $\lambda_D$, surface charge due to the plasma $\sigma_s$, and finally the oxidation rate $R_{\text{ox}}$. A horizontal arrow indicates that the quantity does not depend on the plasma parameter. Below each parameter the corresponding experimental section is indicated.](image)
(Fig. 7.12), we can exclude ozone from being directly and solely responsible for the fast plasma oxidation process.

The charge density at the surface $\sigma_s$ due to the plasma could increase the oxidation rate, as was argued in section 3.4.2. However, it was already estimated that any contribution from this extra charge is probably negligible in a standard glow discharge plasma. It was assumed that the ion density in the plasma was $10^{16} \text{ m}^{-3}$, but in our plasma the ion density is one order of magnitude lower, resulting in an even lower surface charge density. Furthermore, since the surface charge is inverse proportional to the Debye length, the dependence of the surface charge on the plasma power, pressure and distance (Fig. 7.20) does not correlate with the measured behavior of the oxidation rate. We can therefore exclude (under our experimental conditions) the influence of the extra charge due to the plasma.

The inability to explain plasma oxidation rates as being determined by a single particle may point towards an oxidation mechanism in which two or more species are involved, which has not been reported in literature before. In the next section, we will further develop these ideas.

7.8 A novel model for plasma oxidation involving ions and atoms

For the present case of plasma oxidation, there are a number of ways the various species from the plasma can enhance the oxidation process, as has been mentioned in sections 3.4.3, 3.4.4 and 3.4.7. In this section we propose a novel model that uses oxygen ions and atoms to enhance the oxidation rate. We will use as a basis the model of Cabrera (section 3.2.4) for the thermal oxidation of aluminum that leads to the inverse logarithmic growth law. Recall that, in the Cabrera model, the oxidation rate is limited by the rate at which aluminum ions make a thermal hop into the oxide, after which they are pulled rapidly through the oxide causing oxidation at the surface. The activation energy $W$ for the hop is lowered by the field $E = V/l$ over the oxide, which is created by electrons tunneling towards oxygen molecules at the surface. The rate of thermal oxidation of aluminum is

$$\frac{dl}{dt} = \Omega_{ox}^\text{Al} \, N \nu \exp \left( \frac{-W + qaV/l}{k_B T} \right), \quad (7.6)$$

where $\Omega_{ox}^\text{Al} = 2.1 \cdot 10^{-29} \text{ m}^3$ is the volume of oxide formed per oxidized Al ion, $N$ (in m$^{-2}$) is the number of Al ions that are available for movement into the oxide, $\nu$ (s$^{-1}$) is the attempt frequency of Al ions for hopping into the oxide, and $s \propto \lambda_D$, see sections 3.3.2 and 3.4.2.
approximately equal to the lattice vibration frequency, \( q \) is the charge of the ion, and \( a \) is the hopping distance. The factor \( N \nu \) in this expression can be seen as the number of attempts (per m\(^2\), per second) of Al ions hopping into the oxide, whereas the exponent represents the probability that the attempt will result in one ion hop, subsequently followed by oxidation at the surface.

We now conjecture that in the plasma oxidation process both oxygen atoms and oxygen ions have a separate influence on the oxidation mechanism, and that the expression for plasma oxidation rate has a form similar to Eq. 7.6:

\[
\frac{dl}{dt} = \Omega_{\text{ox}}^{\text{Al}} \cdot f(\Gamma_+, l) \cdot P(\Gamma_0, E_+, l),
\]

where \( f(\Gamma_+, l) \) represents the number of attempts (per unit area and unit time), depending on the flux of oxygen ions towards the sample and on the thickness of the oxide, and \( P(\Gamma_0, E_+, l) \) is the probability that an attempt results in bringing one Al ion into the oxide, depending on the flux of O towards the sample, the energy delivered by ions and the thickness of the oxide. We will now discuss the separate contributions of atoms and ions in more depth.

**Oxygen ions**

Oxygen ions can deliver a large amount of energy (more than 20 eV per ion) very locally to the sample surface, as has been discussed in section 3.4.7. This delivery of energy, often called a thermal spike, can be regarded as a very local increase in temperature of some Al ions at the Al/Al\(_2\)O\(_3\) interface, as depicted schematically in Fig. 7.21a. For a short period of time \( \tau_{\text{ts}} \), the higher temperature \( T' \) will directly increase the probability that an affected Al ion will hop into the oxide:

\[
P(E_+) = \exp\left(\frac{-W + qaV/l}{k_B T'}\right),
\]

where \( T' \) is a function of the ion energy \( E_{\text{ion}} \) and the depth \( l \) and is larger than the ambient temperature (room temperature). The thermal spike dissipates away very quickly and can therefore assist ions for only a very short period of time. The number of attempts an ion can make is equal to the lattice vibration frequency (identical to the thermal case) \( \nu \) times the duration of the thermal spike \( \tau_{\text{ts}} \).

The temperature \( T' \) of an Al ion at a depth \( l \) (corresponding to the oxide thickness) due to a thermal spike is of course lower for larger \( l \), since the energy is divided over much more atoms. The simple model that treats heat dissipation macroscopically in a semi-sphere in the oxide, introduced
Chapter 7. Dynamics of the Plasma Oxidation Process

Figure 7.21: The energy (> 20 eV) delivered by an ion spreads in the oxide, locally increasing the temperature of several aluminum ions at the Al/Al$_2$O$_3$ interface. In the right picture, a thicker oxide thickness results in a larger number of significantly affected Al ions.

in section 3.4.7, gives us an expression for the effective temperature at a certain depth $l$:

$$T' = T_{rt} + B_{ts}/l^2,$$

where $T_{rt}$ is the ambient temperature (room temperature) and $B_{ts}$ is a constant, representing the temperature increase due to the thermal spike. Using this simple model, it was estimated that an atom at an oxidized Al thickness of 1 nm could obtain an extra energy$^9$ of the order of 0.08 eV, corresponding to a temperature increase of 900 K, hence $T' \approx 1200$ K!

The number of Al ions at the interface that are significantly affected by a thermal spike ($K$) depends on $l$, as can be seen in Fig. 7.21a and b. At thicker oxide thicknesses, the number of affected Al ions increases, and the probability for each Al ion decreases. Hence, one energetic oxygen ion can assist in the jump of $K$ Al ions into the oxide, with a probability $P(T', l)$:

$$K \nu_{ts} P(T'(E_+, l), l) = K \nu_{ts} \exp \left( \frac{-W + qaV/l}{k_B(T_{rt} + B_{ts}/l^2)} \right),$$

Parallel to this process, natural hopping of Al ions (not assisted by a thermal spike, $T = T_{rt}$) still occurs, but we estimate that for thicknesses above about 0.6 nm the number of Al hops induced by ion impact is much larger. Hence, the ion impact mechanism controls the “number of attempts” of the oxidation process, as did the term $N\nu$ in the expression for thermal oxidation (Eq. 7.6).

$^9$Delivered energy = 10 eV, oxide thickness when 1 nm Al is oxidized is 1.275 nm, see section 3.4.7.
We find an expression for the oxidation rate due to ion impact:

\[
\frac{dl}{dt} = \Omega_{\text{ox}}^{\text{Al}} \Gamma^+ K^n \tau_{\text{ts}} \exp\left(-\frac{W + qaV}{k_B(T_{\text{RT}} + B_{\text{ts}}/l^2)}\right),
\]

where \(\Gamma^+\) is the ion flux, \(K\) is the number of affected Al ions at the Al/Al\(_2\)O\(_3\) interface, \(n\tau_{\text{ts}}\) is the number of attempts each Al ion makes, and the exponent is the probability for each Al ion that an attempt is successful \(i.e.\) resulting in a hop and subsequent oxidation. Hence, the thickness dependence of the ion impact oxidation rate depends on the spreading of the energy of the thermal spike. In Fig. 7.22a the oxidation rate as a function of thickness of a standard measurement is shown, and compared to Eq. 7.11. A rough qualitative correspondence between the measurement and our simple model is found. We note that the macroscopic approximation of the dissipation of energy is probably an oversimplification. Ion impact simulations can give more insight in the exact process of thermal spike stimulated Al ion hopping. For the similar case of 100 eV-Ar\(^+\) impact on a nickel surface, Müller [Mul86] has performed such simulations, and found the jump-probability of a Ni-atom as a function of distance, which is shown in Fig. 7.22b. Although the systems have properties which are probably different, a resemblance to our measurement is clearly emerging, suggesting that our model of thermal-spike induced Al-hopping is correct.

**Figure 7.22:** a) Oxidation rate versus oxidized thickness of a standard measurement (10 Pa, 6 W, from Fig. 7.3), compared with a theoretical oxidation rate determined by Eq. 7.11. b) Simulated effect of the delivery to a Ni layer of 100 eV by an incident argon ion: the number of hops by an atom located at a distance \(r\) from the center of the thermal spike, for several values of the activation energy of the hop. Data taken from [Mul86].
Oxygen atoms

Oxygen atoms, with lower energy surface levels and a higher sticking probability as compared to O\textsubscript{2}, can increase the voltage over the oxide as outlined in section 3.4.3. We neglect the possible influence of ozone, of which the presence might also have an influence on the oxide voltage, or might increase the O density via dissociation at the surface. Since O\textsubscript{2} is present at the surface as well, an “effective voltage” \( V' \) results, which we approximate by an average of the O-voltage and O\textsubscript{2}-voltage. Hence, \( V' \) is a function of the surface coverage by O and O\textsubscript{2}:

\[
V' = V_0 \cdot (\alpha \Theta_{O2} + \beta \Theta_O),
\]

(7.12)

where \( \Theta_i \) represents the fraction of the surface covered by species “i”. The ratio of the O and O\textsubscript{2} densities at the surface depends on the fluxes towards the surface \( \Gamma_O \) and \( \Gamma_{O2} \), the sticking coefficients \( S_O \) and \( S_{O2} \), and the rate of desorption. Consumption of oxygen in the oxidation process is neglected, since a rate of about 1.3 nm/s, the highest rate encountered (Fig. 7.3), consumes about \( 4 \times 10^{19} \) oxygen atoms per second per m\(^2\), whereas the O\textsubscript{2}-flux at 10 Pa is about \( 10^{21} \) m\(^{-2}\)s\(^{-1}\). The flux of atoms is, since the degree of dissociation is roughly 1% (Fig. 7.18), \( 1 \times 10^{21} \) m\(^{-2}\)s\(^{-1}\). We neglect the production of ozone from O + O\textsubscript{2} at the surface as well. Hence, all fluxes from the plasma towards the sample are much larger than the consumption by the oxidation process, see Fig. 7.23.

In steady state conditions, the flux towards the surface balances the rate of desorption:

\[
\begin{align*}
S_O \Gamma_O (1 - \Theta_O - \Theta_{O2}) &= \nu \Theta_O n_0 \exp(-E_O/k_B T) \\
S_{O2} \Gamma_{O2} (1 - \Theta_O - \Theta_{O2}) &= \nu \Theta_{O2} n_0 \exp(-E_{O2}/k_B T),
\end{align*}
\]

(7.13)

where \( E_O \) and \( E_{O2} \) are the energy barriers for desorption, \( \nu \) is an attempt frequency and \( n_0 \) is the total number of sites. The term \( (1 - \Theta_O - \Theta_{O2}) \), representing the fraction of unoccupied sites, makes sure that the surface coverage cannot exceed one monolayer of oxygen.

**Figure 7.23:** Schematic sketch of the fluxes of particles arriving at and departing from the sample surface. The incident O and O\textsubscript{2} fluxes are very large compared to the consumption by the oxidation process and O\textsubscript{3}-production at the surface.
The surface coverage is not known exactly, but in the Cabrera model it is assumed that the surface is practically saturated with oxygen. We can make a rough estimate: in thermal oxidation experiments in 10 to 10000 Pa \(O_2\), Kuiper et al. found that the oxidation rate increases only by a factor of three when the pressure is increased over three orders of magnitude [Kui01a]. Since the oxide voltage is the only “external” variable in the Cabrera model that influences the rate of oxidation, the small variation in oxidation rate is likely to be due to small variations in surface coverage. When looking at the balance for \(O_2\) in Eq. 7.13 (without \(O\) present), we deduce that if a pressure increase \((\Gamma_{O_2} \propto p_{O_2})\) of 3 orders of magnitude has only a small effect on \(\Theta_{O_2}\), then \(\Theta_{O_2}\) must be very close to unity, approximately 0.99 or more.

We conjecture that the effect of the (much smaller) flux of \(O\) atoms is the replacement of \(O_2\) on the surface, resulting in a higher oxide voltage. By dividing the expressions of Eq. 7.13 and using for the flux

\[
\Gamma_x = n_x \sqrt{\frac{k_B T}{2\pi m_x}},
\]

we deduce the ratio

\[
\frac{\Theta_O}{\Theta_{O_2}} = \frac{S_O n_O}{S_{O_2} n_{O_2}} \exp(\Delta E/k_B T) \quad (\Delta E = E_O - E_{O_2}).
\]

Unfortunately, exact values for both sticking coefficients and desorption energies are not available; it is only known that, as has been mentioned in section 3.4.3, atoms have a somewhat higher sticking coefficient and probably a stronger bonding to the surface. Assuming that \(\Theta_O\) is much lower than unity, \(\Theta_O\) is approximately linear with the flux of \(O\) atoms towards the surface. The voltage over the oxide is approximated as an average over the \(O_2\) voltage and the \(O\) voltage, in the low \(O\)-coverage limit linearly depending on \(\Theta_O\):

\[
V' = V_{O_2} + \alpha \Theta_O = V_{O_2} + \alpha' n_O,
\]

where \(V_{O_2}\) is the oxide voltage with only \(O_2\) at the surface, and \(\alpha\) and \(\alpha'\) are constants.

The combined effect of oxygen atoms and ions

Using the ion-driven oxidation rate, and adding the influence on the voltage due to atoms, the expression for the oxidation rate now looks like

\[
\frac{dI}{dt} = \Omega_{ox}^\mathrm{Al} \Gamma_+ K n \tau_{ts} \exp \left( -\frac{W + qaV'/l}{k_B T'} \right)
\]

\[
V' = V_{O_2} + \alpha' n_O,
\]
where $\Gamma_+$ is the flux of ions towards the sample, which is directly proportional to the ion density in the plasma.

Using this model, the oxidation rate can be calculated for a given combination of ion density and oxygen density in the plasma. We will now verify the model by comparing the calculated oxidation rate (at 1 nm oxidized Al), using the ion and atom densities that were measured (sections 7.4 and 7.6), to the oxidation rate measured with the ellipsometer (section 7.2). The effective temperature $T'$ and the constant $\alpha'$ will be used as fitting parameters. Note that the ion energy $E_+$ depends on the accelerating sheath voltage, which is controlled by the electron temperature $T_e$ (section 3.3.2). Since $T_e$ varies only slightly around 2 eV for all plasma conditions, the energy delivered by ions can be considered constant, and hence $T'$ will be the same for all measurements (for a fixed oxide thickness!). We approximate the number of significantly affected Al ions at this thickness by a constant number of 6 (see Fig. 7.21); the hopping probability of atoms that are located further away from the point of impact decreases exponentially with the distance. The “duration” of the thermal spike $\tau_{ts}$ is estimated from simulations of Müller to be about 50 times the lattice vibration period, hence $\nu\tau_{ts} = 50$. For the parameters $W$ and $V$ the values determined in the previous section, 1.3 eV and 1.18 eV, respectively, can be used. Furthermore, $\alpha$ is 0.35 nm as in the original calculations of Cabrera, and the oxide thickness$^{10}$ $t$ is 1.275 nm. The result of the fit is shown in Fig. 7.24.

The fit is reasonably good; the discrepancy of the 10 Pa measurements is due to the spread in the O density measurement, see Fig. 7.18. The effective temperature $T'$ emerging from the fit is found to be 0.12 eV, corresponding to 1370 K, which is slightly higher than estimated with the simple macroscopic model. The other fit parameter, $\alpha'$, is found to be $4.2 \times 10^{-20}$ V. The influence

\[\text{Figure 7.24: The oxidation rate (at an oxidized thickness of 1 nm) as a function of plasma power and pressure. The lines represent the oxidation rate as determined by ellipsometry data (interpolated from Fig. 7.4). The symbols indicate the oxidation rate as fitted using the simple model (Eq. 7.17). Errors are estimated to be 20%, but are not shown for clarity.}\]

10 An oxidized Al thickness of 1 nm corresponds to an oxide thickness of 1.275 nm.
Figure 7.25: Comparison between the ellipsometry measurements with the model of the oxidation rate vs. the separation between the plasma source and the substrate. (The standard distance is 37 mm).

of the oxygen atoms in standard conditions (10 Pa, 6 W, \( n_O = 1.9 \times 10^{19} \)) on the oxide voltage is therefore approximately 0.8 V, increasing the “natural” oxide voltage due to \( O_2 \) (1.18 V) by 70%, and lowering the activation barrier for Al ion hopping from 1.06 eV in the natural case to 0.75 eV in our plasma experiments.

Note that although the quality of the fit is good and the fitted parameters are reasonable, suggesting that our model is correct, a lot is still unclear and needs to be examined, of which the most important is the exact effect of an ion impact. This can be determined via ion-impact simulations similar to Müller’s work.

All parameters (oxidation rate, ion density, atom density) have been measured as a function of the separation between the plasma source and the sample as well (figures 7.5, 7.10 and 7.19). Using these data and the same parameters as were used for the fit in Fig. 7.24 the oxidation rate was calculated and compared with the measured rate of oxidation. This is shown in Fig. 7.25. The calculated rates are somewhat lower than the measured rate. Most likely this is due to the measurement of the O density. The oxidation rate and ion density were measured while the separation between the plasma source and the sample was increased, whereas the O density was measured at various positions between the source and the sample, while keeping the separation between the source and the sample constant. Our assumption that the expected dependence on the distance is similar is apparently not correct.

Summarizing, we have developed a plasma oxidation model based on the original model of Cabrera. The rate of oxidation is influenced by the plasma via two independent processes:

- First, oxygen ions deliver energy to the sample surface in the form of
thermal spikes. Each incident ion can cause one or more Al ions to hop into the oxide, depending on the oxide thickness. As the oxide grows larger, the effect of the thermal spike decreases according to the numerical simulations of Müller.

- Secondly, oxygen atoms enlarge the field in the oxide, which in practice corresponds to lowering the activation energy of the jump of Al ions into the oxide.

7.9 Influence on the tunnel barrier properties

It was mentioned in section 1.3 (Fig. 1.5), that a tunnel junction with a barrier made from a certain amount of Al will have a higher specific resistance when, instead of thermal oxidation, plasma oxidation is used. Furthermore, the TMR of plasma-oxidized junctions is generally higher as well. Now that we have identified the processes that occur during plasma oxidation and established a working model for the plasma oxidation process, we can discuss the difference between plasma and thermally oxidized barriers for magnetic tunnel junctions. Since in this research no actual junctions were made, we will only shortly give some suggestions, leaving the proof to further research.

The thermal spike rearranges the atoms in the oxide

The high amount of very locally delivered energy causes some rearrangement of atoms in the oxide. The oxide structure may become more homogeneous or stoichiometric. However, it has been found by Koller et al. that in plasma-oxidized junctions there is still an asymmetry in the barrier [Kol04b]. Impurities, possibly having a stronger bonding, and defects, may be removed from the oxide.

The plasma oxidation rate is more homogeneous

A tunnel barrier with inhomogeneous thickness will conduct the largest part of the current through the thinnest parts of the barrier since the current depends exponentially on the thickness, see section 1.2.1. From the rate equations of thermal oxidation and plasma oxidation, we will now deduce that, during plasma oxidation, the oxidation rate $R$ depends more sensitively on the oxide thickness as compared to thermal oxidation.

For both the thermal and plasma oxidation process it holds that if some amount of roughness is present (the oxide thickness is not homogeneous), the thinner parts of the barrier will oxidize faster. For plasma oxidation, this effect is much stronger than for thermal oxidation. We have simulated
the difference in oxidation rate between a thin part and a slightly thicker part of an oxide:

\[ \Delta R = \left. \frac{dl}{dt} \right|_t - \left. \frac{dl}{dt} \right|_{t+\Delta t} \]  \hspace{1cm} (7.18)

and normalized this to the oxidation rate \( R \) at the thinnest part. This is shown in Fig. 7.26. From the figure we deduce that if the oxide thickness is 1 nm, a slightly thicker part will have a much lower relative oxidation rate in the case of plasma oxidation with respect to thermal oxidation. Using STM, it was observed by Ando et al. [And02] that indeed plasma oxidation results in an oxide with less roughness than thermally or radical-beam oxidized barriers. In combination with a higher voltage over the oxide due to oxygen atoms from the plasma, pinholes are oxidized faster, decreasing the parasitic non-polarized currents, thereby increasing the TMR of the junction.

7.10 Conclusions and suggestions for further research

In this chapter, the in-situ ellipsometry technique has been used to measure the rate of oxidation as a function of plasma power and pressure. It has been established that the oxidation rate increases directly with both the plasma power and plasma pressure. Using various plasma characterization techniques, the most important properties of the plasma, ion density, electron temperature, ozone density and O density, were measured as a function of plasma power, pressure and distance to the plasma source. The fluxes of these particles to the sample surface were compared to the oxidation rates, and it was concluded that the fast plasma oxidation is not governed by one single species.

**Figure 7.26:** The normalized difference in oxidation rates at thicker and thinner parts of the oxide layer, if a small roughness is assumed.
Using these observations, we developed a plasma oxidation model (based on the original model of Cabrera) in which the rate of oxidation is influenced by the plasma by two independent processes: the first process that plays an important role in the plasma oxidation process is the delivery of energy to the Al/Al$_2$O$_3$-interface by oxygen ions in the form of thermal spikes. It was found that each incident ion has a certain probability to assist one or more Al ions to hop into the oxide. As the oxide grows larger, this probability decreases, since the heat of the thermal spike is divided over an increasing amount of atoms. The exact thickness dependence could not be deduced analytically, but simulations of 100 eV-Ar$^+$ impact on Ni suggest a thickness dependence that is remarkably similar to the dependence that is observed. Similar simulations of 20 eV O$_2^+$ impact on an oxide surface should give more insight and better predictions for the thickness dependence of the rate of oxidation.

The second effect that increases the rate of oxidation is related to oxygen atoms that enlarge the field in the oxide, which in practice corresponds to lowering the activation energy of the jump of Al ions into the oxide. Since the exact effect of O atoms is unknown, experiments should be performed to measure the sticking coefficient and electronegativity at the surface of both O and O$_2$.

In order to verify the model, we calculated the oxidation rate from the measured fluxes of O$_2^+$ ions and oxygen atoms as determined by Langmuir probes and actinometry, respectively. The good correspondence to the actual oxidation rate, measured by ellipsometry, suggests that our model gives a good description of the plasma oxidation process of aluminum layers.
Chapter 8

Atomic Layer Deposition

8.1 Introduction

Atomic Layer Epitaxy (ALE), Atomic Layer Deposition (ALD) or Atomic Layer Chemical Vapour Deposition (AL-CVD) is a class of surface controlled methods of producing atomic surface layers, epitaxial films, and ultra thin films [Bed94, Sun94]. Originally developed as ALE in the 70’s by Suntola [Sun77] for manufacturing electroluminescent displays, the technique was soon adapted for thin gate dielectrics for complementary metal-organic semiconductor (CMOS) devices and dynamic random access memory (DRAM). The main advantages of this technique, as will be shown in the text below, are a theoretically perfect control of the deposited layer thickness and a very good uniformity and conformity. Additionally, ALD is being advertised as a technique which produces layers with an extremely low pinhole density. These advantages make ALD in principle the perfect method for creating ultra-thin barrier layers for magnetic tunnel junctions. In this chapter the ALD technique is shortly explained, and measurements on samples made by CVC/Veeco in Fremont, California, are discussed.

8.2 Principle of ALD

Atomic layer deposition is a process similar to chemical vapor deposition (CVD). In CVD, two gases are let into the deposition chamber and react at or above a surface to create a compound layer.

ALD differs from CVD at only one point: the two reactive gases do not enter the chamber continuously and simultaneously, but are let into the chamber in a cycle of alternating pulses of the two gases. If the precursors and the substrate are chosen well, the process is divided in two well-defined separate surface reactions. A cycle of an exemplary process to make a com-
pound AB from two precursors AX and BY is shown in Fig. 8.1 and consists of the following steps:

1. In a vacuum chamber, a flow of AX is guided over a substrate with B-atoms at the surface. AX reacts with the surface, forming BAX. The combination of AX and B is chosen such that only BAX is formed, and that the reaction stops when the surface is saturated.

2. An inert gas (Ar, He, N\textsubscript{2}) is used to purge the chamber.

3. The second precursor, BY is let into the chamber. It produces AB, and all the X is removed from the surface. This molecule BY is chosen such that the reaction stops after a single layer and leaves a B-surface, which is the same surface with which the cycle started with.

4. Another round of purging gas is used to clean the chamber again, and the surface is ready for the next cycle.

In formula, the two reaction steps are

\[ B(s) + AX(g) \rightarrow BAX(s) \]  \hspace{1cm} (8.1)

and

\[ BAX(s) + BY(g) \rightarrow BAB(s) + XY(g), \]  \hspace{1cm} (8.2)

where s and g denote solid and gas phase, respectively. Since the process is surface-controlled and self-limiting, the thickness of the resulting film depends in principle only on the number of cycles, giving exact thickness control. Practice proves not to be so ideal, as will be shown in the next section.

The conformity is also very good as opposed to molecular beam epitaxy, since it has no direction of deposition - the gas fills the entire chamber and covers every surface, whereas sputtering gives a coverage of the bottom of a trench, but leaves the vertical walls free, as in Fig. 8.2. It was shown
by Bubber et al. that indeed ALD of Al\textsubscript{2}O\textsubscript{3} in trenches of 100 nm wide and 1 \textmu m deep gives a perfect 100\% coverage of walls and bottom of the trench [Par01a].

Deposition is usually done at an elevated temperature between 100 °C and 1000 °C, depending on the chosen precursors, in order to stimulate the surface reactions. If the temperature is too high, dissociation of precursors might occur, which means that the surface is not ready for the next step in the cycle. Another negative effect at higher temperatures is that the desorption rate might be higher than the reaction rate, and hence saturation of the surface will not occur. On the other hand, if the temperature is too low, the sticking might be so high that more than one monolayer forms. However, the temperature window in which good layers are formed is not very small (as compared with MBE), hence the deposition temperature is not extremely critical. This can be a serious advantage for industrial processes since this enhances the throughput of wafers. It must be emphasized again that all depends on the correct choice of combination of precursors and substrate.

8.3 Aluminum oxide

As mentioned above, the combination of the precursors and the (termination of the) substrate must be chosen such that each step is self limiting to one monolayer, and that the correct reactions take place leaving the proper surface for the next step. See for example [Les99] for combinations of precursors for various materials, from which table 8.1 is a small excerpt.

Various combinations of precursors are used to create Al\textsubscript{2}O\textsubscript{3} layers. Trimethylaluminum (TMA) and AlCl\textsubscript{3} are the most commonly used precursors for aluminum, and H\textsubscript{2}O and ozone are most frequently used as precursors for oxygen. In general, the substrate temperatures can be as low as 150 or 200 °C [Par01a, Bub02] The ALD process using a combination of TMA and H\textsubscript{2}O is discussed using Fig. 8.3. Starting with a surface which is terminated in -OH bonds, TMA is let into the chamber until one monolayer coverage is reached (Fig. 8.3 a and b). In the surface reaction, TMA loses one methyl group, which forms methane (CH\textsubscript{4}) with an H-atom from an –OH-group,
and exits the chamber. The molecule is bonded by the Al-atom, with two dangling methyl groups. In this picture one can already see that a problem is encountered: the coverage can never be complete because of the large dangling methyl groups. This effect is called *steric hindrance*, and it hinders the ideal reaction steps, causing the deposition rate to be less than the ideal case of one monolayer per reaction cycle\(^1\).

\(^{1}\)See for example [Hig89], where the reported deposition rate is half a monolayer per cycle.

![Figure 8.3: The steps of the TMA/H\(_2\)O process to form Al\(_2\)O\(_3\).](image)

<table>
<thead>
<tr>
<th>Precursor 1</th>
<th>Precursor 2</th>
<th>Material grown</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl(_3)</td>
<td>H(_2)O</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td></td>
<td>NH(_3)</td>
<td>AlN</td>
</tr>
<tr>
<td>TaCl(_5)</td>
<td>H(_2)O</td>
<td>Ta(_2)O(_5)</td>
</tr>
<tr>
<td>Al(CH(_3))(_3) (=TMA)</td>
<td>H(_2)O</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>GaCl</td>
<td>AsH(_3)</td>
<td>GaAs</td>
</tr>
<tr>
<td>CuCl</td>
<td>H(_2)</td>
<td>pure Cu</td>
</tr>
</tbody>
</table>

**Table 8.1:** A small list of combinations of precursors to show what is possible with ALD. Besides metal-nonmetal compounds, only a few other types of materials can be grown using ALD, such as pure materials like Cu and Si.
In the next step, water vapor is let into the chamber, which reacts at the surface with the methyl groups: one H-atom of the water molecule and a methyl-group of the surface form gaseous methane, leaving the rest of the water molecule (an OH-group) at the surface. After this reaction step has ended, the surface will look like depicted in e or f. It must be noted that the figure is two-dimensional; the effect of steric hindrance appears to be worse than it is in the real three-dimensional case. After this step, the surface is -OH-terminated again, and the next cycle can be started with TMA.

8.4 ALD-Al$_2$O$_3$ for MTJs

For a material to be used as tunneling barrier in a magnetic tunnel junction, it must have a high specific resistivity (i.e. a low leakage current via pinholes or impurities) and a high breakdown voltage, roughly higher than $10^{10}$ Ω·cm and 5 MV/cm, respectively. For Al$_2$O$_3$-layers made by ALD of 40 nm, very high resistivities of $10^{12}$ Ω·cm are reported by Higashi [Hig89]. Such a resistivity would give a leakage current much less than a tunneling current. The breakdown voltage reported by the same group of more than 8 MV/cm is also sufficient for magnetic tunnel junctions. Aluminum oxide made by ALD is therefore an interesting alternative for plasma-oxidized aluminum, with an additional advantage that the thickness control is perfect, as already mentioned in the introduction of this chapter.

Bubber et al. [Bub02], have deposited ALD-Al$_2$O$_3$ layers in full junction structures (CoFe/AlOx/CoFe/IrMn), using water vapor and TMA as precursors. The other layers were DC magnetron sputtered. They find that the thickness control of ultra-thin layers is not as good as expected, which is probably due to the absence of a suitable initial surface, which is CoFe instead of an OH-terminated surface. This means that during the first few ALD-cycles (“incubation” period), layer growth is not ideal, and only after a few monolayers the thickness increases proportional to the number of cycles.

They report that, in thick layers, high breakdown strengths of over 9 MV/cm were found, together with leakage currents much lower than the tunneling current. For electrical transport measurements, structured MTJs were created with ALD barrier layers of 0.5 to 2.5 nm and junction areas down to 10 μm$^2$. The junctions showed very low resistances (in the range one Ω to a few kΩ) and linear IV-curves, indicating Al-rich barriers and a conductance likely through pinholes instead of tunneling. Junctions of which the ALD-barrier was treated with a high-power Ar:O-plasma showed higher resistances of several MΩ, and non-linear IV-characteristics, indicative of tunneling. Above 0.7 nm the layers are not magnetically coupled, from which it is concluded that there are no pinholes in those layers. They observe a magnetic thickness loss (magnetic material that has become non-magnetic)
of about 0.1 nm at the NiFe/AlOx and CoFe/AlOx interfaces. Nevertheless, no magnetoresistance could be measured in any junction. Probably the lack of success is due to the “incubation layers” of the ALD-process, which “dammages” the bottom electrode too much, i.e. the bottom electrode is slightly oxidized. This “damage” is also seen in the case of deposition of Al₂O₃ on pure Si, where a few layers of SiOₓ were formed at the interface [Fra03]. In the case of the post-processed samples the additional plasma-oxidation makes the damage even worse, of course.

Han et al. used a method in which an Al₂O₃ layer is grown in cycles of subsequent sputter deposition of Al and thermal oxidation [Han04a]. This method was named Pseudo-Atomic Layer Deposition, but it may be obvious that it does not resemble the ALD processes discussed here since the individual steps are not self-limiting. Working MTJs were produced, but the measured values of TMR were geometrically enhanced due to the combination of low $R \times A$ product and large junction area (see [vdV99]).

8.5 Measurements

In order to study the structure and magnetic behavior of ALD-based MTJ-layers in more detail, samples with ALD-Al₂O₃ barriers were deposited at Veeco/CVC in Fremont. Measurements using MOKE, NMR and SQUID are discussed in this section.

8.5.1 Samples

The samples were designed to investigate some important aspects of typical MTJ-layers, in particular magnetic coupling between the electrodes, deterioration of the magnetic layers next to the ALD-layer, and quality of the ALD-Al₂O₃-layer. The barrier was deposited using ALD, the other layers were sputtered using a DC magnetron source. Series 1 is intended to investigate the damage that the two most common precursors, water vapor and ozone, cause to the underlying magnetic electrode. In this case Co is used as bottom electrode, because this is best suited for NMR-experiments.

Series 2 is a complete junction stack including anti-ferromagnetic PtMn in order to pin the bottom electrode [Lee03]. Via magnetization measurements on these layers, we can determine the presence of magnetic coupling between the electrodes. The strength of the coupling, its temperature dependence, and its thickness dependence may give information something about the quality of the ALD-barrier. Moreover, these measurements may give information about the nature of the coupling, e.g. coupling by pinholes versus magneto-static coupling (Néel or “orange peel” coupling, see e.g. [vdH98]).
8.5. Measurements

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Figure 8.4: The sample stacks. In series 1 the Co-thickness is varied in order to study the Co/Al₂O₃ interface; in subseries 1a water is used as precursor for oxygen, in 1b ozone was used. In series 2 the nominal Al₂O₃ thickness is varied. All numbers are nm.

8.5.2 Results

NMR

The cobalt layers in samples of the 1-series were measured using NMR in order to see differences in the amount of magnetically dead material² for two different precursors, water and ozone [Wie03]. To quantitatively determine this amount, the thickness of the cobalt layer was varied. It was found that there is practically no difference between the samples with the water or ozone precursors. Therefore, only the measurements on the water-samples are shown.

In Fig. 8.5 the NMR spectra for the samples with layers of 3.0 and 5.0 nm Co under the ALD-alumina are shown. The area on the left, below 207 MHz, is due to Co with an incomplete coordination, i.e. located at an interface. It is assumed that the interface is identical for all layers, therefore the other graphs are scaled such that these regions overlap³. The right peak represents the cobalt in the hcp-phase, combined with stacking faults, and the left peak represents cobalt in the fcc-phase. We can immediately see that the cobalt initially grows predominantly in a mixed phase of fcc and hcp, but that additional cobalt grows in an fcc phase. The sample with the 10 nm thick Co (not shown here) had different magnetic properties because of which the measurement could not be rescaled reliably. This is more generally seen in thick layers, see for example [Pan97]. It appears that the growth continues to be pure fcc. Although this is an interesting type of growth because it is not observed often, it is not the subject of this work.

²The material that does not add to the magnetic moment of the layer, and supposedly has a negative influence on the tunnel current as discussed in the introductory chapter.

³This is not trivial, since the chemical reactions may be different for hcp and fcc surfaces. However, for Co, the difference between hcp and fcc structures is small and no significant difference could be found in the measurements of the interfaces.
Figure 8.5: NMR measurements on the ALD samples 1: 3.0 nm and 5.0 nm Co.

The amount of magnetically dead material can be estimated if the total intensities are compared with the nominally deposited amounts of Co: it was found that the ratio between the area’s is $0.60 \pm 0.05$, which matches the ratio of the nominal deposited layers: $3.0 \text{ nm}/5.0 \text{ nm} = 0.60$. This indicates that there is probably less than one monolayer of dead material.

From the fraction of the interface area (below 207 MHz) compared with the total area, a thickness of about 0.6 nm is found. This is the combined effect of interface roughness and intermixing of both interfaces. A perfect flat interface would give 0.15 nm of interface-signal per interface [Pan97], which means that in this case there is an interface roughness/intermixing of 0.3 nm, which is 1-2 monolayers. This experimental value of 0.6 nm is comparable to sputtered layers.

**MOKE and SQUID**

The samples of the 2-series, with the PtMn exchange-biassing and various barrier thicknesses, have been measured with MOKE (see section 4.7) at room temperature after an annealing step of 90 minutes at 275°C in 0.14 T. The resulting magnetic hysteresis loops are plotted in Fig. 8.6. The top two loops, for the thickest barriers, show two different switches of layers: one of the free top layer, with a switching field of $5.0 \pm 0.5$ mT, and one of the pinned bottom layer, with a switching field of around 30 mT. In these samples, the magnetic layers are not (strongly) coupled. In the two bottom loops, however, both layers switch their magnetization direction together,
which implies a strong coupling between those layers.

As a first remark, it must be noted that the exchange effect on itself is not very good in these layers; in the ideal case the exchange field\(^4\) is larger than the coercive field\(^5\), which is not the case here. This is perhaps due to the annealing temperature of 275°C which might be too low, although in literature often 240°C is used [Yan03].

Our MOKE-set-up was not able to do measurements at low temperatures, hence it is less suitable for investigating the nature of the coupling or the amount of dead material. These samples have therefore also been measured at various temperatures using a SQUID (section 4.7). Measurements at temperatures from 5 K to 300 K are shown in Fig. 8.7 and Fig. 8.8, for samples with the 0.5 nm oxide layer and the 1.5 nm oxide layer. As a first conclusion from Fig. 8.7, it is obvious that there is a very strong coupling in the 0.5 nm sample, and that in the 1.5 nm sample the two magnetic layers are not strongly coupled. This agrees with the MOKE-measurements.

In Fig. 8.8, the coercive fields and exchange fields are plotted versus the temperature, for the two samples. From Fig. 8.8b we can see that the coercive field of the pinned layer in the non-coupled sample is larger than the coercive field of both layers together in the coupled sample. This

\(^4\)Exchange field (\(H_{eb}\)): shift of the hysteresis loop, see Fig. 1.2.
\(^5\)Coercive field (\(H_c\)): half width of the hysteresis loop, see Fig. 1.2.
Figure 8.7: SQUID measurement data on annealed samples of the 2-series: the full junction stacks. Plots a-c: measurements on the sample with 0.5 nm Al₂O₃. d-f: measurements on the 1.5 nm Al₂O₃ sample.

can be understood by considering both ferromagnetic layers in the coupled sample as one thick layer: in ultrathin layers the largest contribution to the coercive field comes from imperfections at the interfaces. Hence, with increasing thickness, the influence of the interface part decreases. See for example [vdH98].

The temperature dependence of the coercive field and exchange field of the pinned layer in both samples can be understood by assuming that the interface consists of an ensemble of exchange paths, each with its own ordering temperature, giving an average behavior depending on the temperature. This is a strong indication that the layers under investigation have a grain-like structure.

Figure 8.8: SQUID measurement data on annealed samples of the 2-series: the full junction stacks. The exchange fields are compared in the left graph, the coercive fields are compared on the right.
As mentioned before, from temperature dependent measurements of the coupling field, the nature of the coupling can in principle be deduced. In particular, it is interesting to know whether the coupling is due to pin-holes (which, obviously, is not desired) or caused by the magnetostatic effect (which would imply some roughness at the interfaces and a very homogeneous barrier). The coupling energy of the latter type is [Lee02]

\[ E_{ms} = C \, M_P \, M_F \, \exp \left( \frac{-2\pi \sqrt{2} \, t_s}{\lambda} \right), \]  

(8.3)

where \( M_P \) and \( M_F \) are the magnetization of the pinned layer and free layer, respectively, \( t_s \) is the thickness of the barrier layer and \( C \) and \( \lambda \) are material and roughness parameters. This energy does not directly depend on the temperature, but only via the magnetizations \( M_P \) and \( M_F \). These magnetizations depend only weakly on the temperature in the temperature range considered (far below the Curie temperature, which is 980 K for bulk CoFe\( ^6 \)). Also from the measurements it can be seen that the saturation magnetization does not change with the temperature. This excludes Néel coupling from causing the two ferromagnetic layers to be coupled so strong.

Another type of coupling exists via the Ruderman-Kittel-Kasuya-Yosida interaction. RKKY coupling is mediated via conduction electrons, which might occur through a non-magnetic pinhole (an Al-“bridge”) between the two ferromagnetic layers. This type of coupling depends in principle on temperature [Lee02]. However, RKKY-coupling has only been observed in well-defined structures with very smooth interfaces. The strength of this coupling oscillates with the thickness of the spacer layer [Lee02], hence we expect that it averages to zero in the case of the relatively rough interfaces of the layers under consideration. Furthermore, aluminum pinholes are unlikely in this case since any metallic aluminum would oxidize practically immediately under the influence of the water precursor.

Coupling through magnetic pinholes is likely to occur in this system. Such a coupling is basically a direct magnetic contact between the electrodes and could give a ferromagnetic coupling between the layers. In principle the strength of the coupling has the same temperature dependence as the Néel coupling, via the magnetization of the ferromagnetic layers. The coupling through a magnetic pinhole, however, is a complex part, and probably depends on the temperature.

In conclusion, this analysis suggests that the coupling is very likely through magnetic pinholes. This means that the Al\(_2\)O\(_3\) layer is not closed for the thicknesses for which the coupling is strong, i.e. 0.5 and 1.0 nm.

\(^6\)In one study, a lower \( T_C \) of 675 K was found. This is still high enough to neglect the temperature dependence below room temperature.
8.6 Discussion, conclusions, recommendations

From our measurements it can be concluded that in the samples with an Al$_2$O$_3$ barrier made by ALD, a significant magnetic coupling exists over barriers with a thickness of 1.0 nm and less. The coupling in these layers is probably caused by magnetic pinholes, implying that the Al$_2$O$_3$ layers deposited by ALD are not closed. The magnetic thickness loss is less than 0.1 nm and the intermixing/interface roughness is of the order of 1-2 mono-layers. It can also be concluded that there is no difference in using ozone or water vapor as precursor for oxygen.

Combined with the results from measurements of Veeco so far, the future of ALD-Al$_2$O$_3$ barriers for MTJ’s seems not very promising. Promises of the extremely low pinhole density and homogeneity are not fulfilled in these structures, because of which very thin closed layers cannot be grown. In the structures with thicker barriers that are closed and have a low pinhole density, the bottom electrode probably has been damaged (i.e. chemically altered or oxidized) due to the deposition process, which is aggressive in nature. Furthermore, in the range of thicknesses interesting for MTJ’s (between 0.5 and 2.5 nm), the ultimate thickness control is absent due to the incubation layers.

The application of the ALD-technique to MTJs is not very likely unless precursors that do not damage the bottom electrode are found. In order to prevent this damage in another way, deposition of a thin protecting layer on the bottom electrode can be considered. However, this would defeat the advantage of the perfect thickness control that ALD normally has.
Appendix A

Reported Results on MTJs

In this appendix, the TMR and RxA product results of MTJs with aluminum oxide barriers made by various methods in various research groups have been collected. The data are plotted in Fig. A.1 and the references are summed up in table A.1.

Figure A.1: TMR versus the RxA product of junctions containing aluminum oxide, made by various production techniques. The big and small circles indicate the group of plasma and thermally oxidized junctions respectively. For the underlying data including references, see table A.1.
<table>
<thead>
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<th>Method</th>
<th>TMR(%)</th>
<th>RA($\Omega\mu m^2$)</th>
<th>Ref.</th>
<th>Year</th>
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<td>[Che00]</td>
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</tr>
<tr>
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</tr>
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<td>2002</td>
</tr>
<tr>
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Table A.1: Collected Results
Appendix B

Numbers

B.1 Indices of refraction

The index of refraction for light with a wavelength of 630 nm (2 eV) [Wea75]:

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<td>7.479</td>
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<tr>
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<td>0.0</td>
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<td>1.99</td>
</tr>
</tbody>
</table>

B.2 Numbers on Al and Al$_2$O$_3$, Co and CoO

For the materials used in this thesis, the specific masses and thickness ‘conversions’ between Al and Co and their oxides are shown, as are the escape depths calculated from reference [Sea79]. The escape depth of CoO could not directly be found and therefore the escape depth of NiO was used instead. The uncertainty of the escape depths is estimated to be 5 to 10%.

<table>
<thead>
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<th></th>
<th>density (kg m$^{-3}$)</th>
<th>$M$ (g/mol)</th>
<th>$\lambda$(Mg K$\alpha$)</th>
<th>$\lambda$(Al K$\alpha$)</th>
</tr>
</thead>
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<td>102</td>
<td>1.48</td>
<td>1.62</td>
</tr>
<tr>
<td>Co</td>
<td>6400</td>
<td>59</td>
<td>0.8</td>
<td>0.98</td>
</tr>
<tr>
<td>CoO</td>
<td>8900</td>
<td>74.9</td>
<td>0.92</td>
<td>1.12</td>
</tr>
</tbody>
</table>

From these data it is calculated that a layer of 1 nm Al will become 1.275 nm Al$_2$O$_3$ after oxidation, and the oxidation of a layer of 1 nm Co will result in a layer of 1.77 nm of CoO.
Appendix C

Langmuir Probe - Characteristic Equations

Let us consider the type of Langmuir probe method that is most commonly used: a double probe system, consisting of two identical electrodes, separated from each other in the plasma. See for a simplified electrical scheme figure C.1.

At the moment it is neglected that, if the potential difference becomes very large, extra ionization can take place in the sheath. This is unwanted, since the plasma will be disturbed by this. For the same reason, the electron emission (thermionically or by secondary emission) by the electrodes is also neglected.

![Figure C.1: The Double probe system; $V_a$ and $I_s$ are the applied potential and the measured current.](image)

A sheath region (see sec. 3.3.2) will develop above the surface of each electrode, as in figure C.2a. The electrodes are at a negative potential with respect to the plasma, repelling electrons and attracting positive ions. The net current is zero since the probes are symmetric.

If a voltage is applied to the electrodes, say positive to probe 1, electrons will be repelled less and positive species will be attracted less. The total current, $I_s$, consists of electron currents and ion currents to both probes, where ions arriving at a probe surface will be neutralized by getting an elec-
tron from the probe. We are dealing with a floating system (not grounded), so the net current must equal zero:

\[ I_{+1} + I_{e1} = -(I_{+2} + I_{e2}), \]  

(C.1)

where \( I_{+1}, I_{+2} \) and \( I_{e1}, I_{e2} \) are ion currents and electron currents respectively to probes 1 and 2. (If \( I_{+1} + I_{e1} > 0 \), then \( I_{+2} + I_{e2} < 0 \)). The potential distribution in a double probe system is drawn schematically in figure C.2.

\( V_1 \) and \( V_2 \) are the potentials of probes 1 and 2 with respect to the plasma in its direct surroundings, \( V_p \) is called the plasma potential. The potential difference \( V_{bc} \) can appear when the probes are not in the same plasma conditions: the plasma potential at the site of the probes then differs. In general, the probes are at lower potential with respect to the plasma, due to the difference in mobility between electrons and ions: Electrons have a much higher velocity and will therefore charge a surface negative. This charge sets up an electric field that repels more electrons and attracts positive ions. An equilibrium settles, leaving the probes at a lower potential with respect to the plasma.
A typical I-V-characteristic is shown in figure C.3. For not too high applied potentials (in the figure between B and C), the ion currents vary only slowly with changes in $V_1$ and $V_2$, because all ions that arrive at the edge of the sheath around the probe are accelerated towards it, so the ion current can only increase if the collecting area (the sheath surface) increases. The changes in current are due to the electrons: one probe becomes more positive, attracting more electrons, the other one becomes more negative, repelling more electrons. For $V_a$ lower than $V_p$, electrons are repelled, but a fraction, equal to a Boltzmann factor

$$I_{e1} = i_{e1}A_1e^{eV_1/T_e},$$  \hspace{1cm} (C.2)

has enough energy to overcome the potential and reach the probe anyway. Here, $i_{e1}$ is the random electron current density in the neighborhood of the probes, $A_1$ is the probe surface and $T_e$ is the average electron energy (in electronvolts). Therefore a small change in $V_a$ can give an exponential increase in electron currents. This last statement holds in most cases, but equation C.2 holds of course only if the electrons have a Maxwellian distribution. If $V_a$ is increased, at point C in figure C.3 probe 2 is so negative, that no electrons can reach the probe anymore. Equation C.1 thus becomes:

$$I_{+1} + I_{+2} = -I_{e1}.$$  \hspace{1cm} (C.3)

At this point, increasing $V_a$ leads to probe 2 becoming more negative, but no increase in electron current (because it is already zero). This part of the IV characteristic is known as the saturation region, but real saturation ($dI/dV = 0$) does not occur normally: When the probe becomes more negative, the sheath will increase, and (e.g. for a cylindrical probe) the sheath-area grows and will gather more positive ions. Only if the ratio of the radius of such a probe and the Debye length approaches infinity can real saturation take place. Also finite (small dimensions compared to $\lambda_{Debye}$) flat probes won’t show real saturation but only a change in slope. In the ideal case, the system is symmetrical so the same holds for the other probe, for negative $V_a$. An asymmetry can be caused by differences in the plasma at the positions of the probes or by different probe dimensions. In figure C.3 the effect of such an asymmetry is plotted: the IV-curve is in this case slightly shifted up and to the right.

As said, in the presented model a Maxwellian energy distribution of the electrons was assumed. The electron current towards the probe for a voltage $V_1$ ($< 0$), is given by equation C.2. Using relation C.1 we obtain a relation for the sum of the ion currents:

$$I_{+1} + I_{+2} = \Sigma I_+ = - \left[ i_{e1}A_1 \exp \left( +\frac{V_1}{V_e} \right) + i_{e2}A_2 \exp \left( +\frac{V_2}{V_e} \right) \right],$$  \hspace{1cm} (C.4)
Appendix C. Langmuir Probe - Characteristic Equations

with \( V_e(V) = kT_e/e \) (V) \( \equiv \hat{T}_e \text{ (eV)} \). This can be rewritten as:

\[
\Sigma I_+ = -I_{e1} \left[ 1 + \frac{i_{e2}A_2}{i_{e1}A_1} \exp \left( \frac{V_{bc} - V_a}{V_e} \right) \right].
\] (C.5)

where we used \( V_1 - V_2 = V_a - V_{bc} \) from figure C.2. If the probe areas are equal and \( I_{+1} \) and \( I_{+2} \) are independent of the potential (large probe with respect to \( \lambda_{\text{Debye}} \)) then a simple equation for the IV characteristic can be derived:

\[
I_s = I_+ \left[ \frac{\exp \left( \frac{V_{bc} - V_a}{V_e} \right) - 1}{\exp \left( \frac{V_{bc} - V_a}{V_e} \right) + 1} \right] = I_+ \tanh \left( \frac{V_{bc} - V_a}{2V_e} \right).
\] (C.6)

In this case, real saturation takes place, and with \( I_s = I_+ \) at large \( V_a \) one can easily determine \( V_e \):

\[
\left[ \frac{dI_s}{dV_a} \right]_{I=0} = -\frac{I_+}{2V_e}.
\] (C.7)

When there is no real saturation, it is necessary to make an assumption: we assume the ion current varies linearly with the probe potential [Swi70, page 142]:

\[
I_{+1} = A_1i_{+1} - S_1V_1,
\] (C.8)

and similar for the ion current to probe 2, where \( S \) is a parameter. The current in the system will now be:

\[
I_s = A_1i_{+1} - SV_1 + I_{e1}
\]

\[
= -[A_2i_{+2} - SV_2 + I_{e2}].
\] (C.9)

Differentiating with respect to \( V_a \) gives:

\[
\frac{dI_s}{dV_a} = \left( -S + \frac{I_{e1}}{V_e} \right) \frac{dV_1}{dV_a} = \left( S - \frac{I_{e2}}{V_e} \right) \frac{dV_2}{dV_a}
\] (C.10)

\[
\frac{d^2I_s}{dV_a^2} = + \left( \frac{I_{e1}}{V_e^2} \right) \left( \frac{dV_1}{dV_a} \right)^2 + \left( -S + \frac{I_{e2}}{V_e} \right) \frac{d^2V_2}{dV_a^2}
\]

\[
= - \left[ \frac{I_{e2}}{V_e^2} \left( \frac{dV_2}{dV_a} \right)^2 + \left( S - \frac{I_{e1}}{V_e} \right) \frac{d^2V_1}{dV_a^2} \right],
\] (C.11)

and the derivatives of \( V_1 - V_2 = V_a - V_{bc} \) (from figure C.2) are:

\[
\frac{dV_1}{dV_a} = 1 + \frac{dV_2}{dV_a}
\] (C.12)
and
\[ \frac{d^2V_1}{dV_a^2} = \frac{d^2V_2}{dV_a^2}. \] (C.13)

Adding the two equations in C.11 gives
\[ \frac{2d^2I_s}{dV_a^2} = \frac{I_{e1} - I_{e2}}{V_e} \left[ \frac{d^2V_1}{dV_a^2} + \frac{1}{V_e} \left( \frac{dV_1}{dV_a} \right)^2 \right] - \frac{I_{e2}}{V_e} \left[ 1 - \frac{2dV_1}{dV_a} \right]. \] (C.14)

The first term here vanishes when the electron currents are equal, the so-called point of inflection (designated by the $i$), and from equation C.10:
\[ \frac{dV_1}{dV_a} = -\frac{dV_2}{dV_a}. \] (C.15)

Combining this with C.12:
\[ \frac{dV_1}{dV_a} = \frac{1}{2}; \quad \frac{dV_2}{dV_a} = -\frac{1}{2}. \] (C.16)

And with this equation we find that also the second term in C.14 becomes zero, hence $d^2I_s/dV_a^2 = 0$ when the electron currents are equal. From equation C.10 the mean electron energy $V_e$ can be determined in the following way. For this equation it is necessary to get the electron currents at the point of inflection:
\[ I_{e1i} + I_{e2i} = -\left[ I_{+1i} + I_{+2i} \right], \] (C.17)
so each electron current at this point is half this value. From formula C.8:
\[ I_{+1i} + I_{+2i} = I_{+1sat} + I_{+2sat} - 2S\Delta V, \] (C.18)
where $\Delta V$ is the change in $V_a$ from the point of inflection to the saturation region (where the electron current is zero). The derivation [Swi70, pag. 144-147] of the relation between $\Delta V$ and $V_a$ is complex and only the result will be given here:
\[ \Delta V = 0.85V_a. \] (C.19)

We now obtain
\[ I_{e1i} = I_{e2i} = -\frac{1}{2} \left( I_{+1sat} + I_{+2sat} - 1.70S\Delta V_a \right). \] (C.20)

With these four expressions and equation C.10 at the point of inflection we get the final expression for $V_e$:
\[ V_e = -\frac{I_1 - I_2 - 1.70S\Delta V_a}{2(2 \frac{dI_s}{dV_a}|_{i} + S)}. \] (C.21)
Unfortunately, the point of saturation cannot be seen very clearly, and often it is a smooth transition. The following procedure gives a good approximation. The necessary parameters can be obtained from an IV characteristic as shown in figure C.4. For $S$ the average of the derivatives for negative and positive $V_a$ is taken. The point of inflection cannot always be determined exactly, but normally it is taken at $I_s = 0$. The electron density $n_e$ can also be determined from parameters in this figure and the electron temperature. At the saturation point, all ions that happen to come at the collecting surface actually add to the ion current. The effective current towards a surface with area $A$, if the particles have a Maxwellian energy distribution, is:

$$I_+ = 0.6n_{edge}eA\sqrt{\frac{kT_e}{m_+}}.$$  \hfill (C.22)

For $A$ one should use the total collecting area: the surface of the sheath. The factor 0.6 is a factor that takes into account the finite size of the probe\cite{Swi70, pag. 113-115}. Unless the Debye length is large, one can take the probe surface as the collecting area. $m_+$ is the mass of the accelerated ions. Often, the plasma consists of more than one ionized species, and in this case the ion mass has to be assumed\footnote{This could be determined roughly by spectroscopy}. The ion density (in the undisturbed plasma, away from the probes) follows easily:

$$n_+ = \frac{\frac{1}{2}(I_1 + I_2)}{0.6eA_p\sqrt{cT_e/m_+}}.$$  \hfill (C.23)

If the ionized atoms are all singly charged, the electron density is equal to the ion density.
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Abstract

Magnetic tunnel junctions (MTJs) are electrical devices that display a large change in resistance when an applied magnetic field switches direction. MTJs are potentially applicable as a non-volatile memory element in Magnetic Random Access Memory (MRAM), potentially decreasing the energy consumption and allowing for instant-on operation of personal computers.

Magnetic tunnel junctions consist of two ferromagnetic metallic electrodes, separated by an insulating layer with a thickness in the order of 1 nm. If a voltage is applied over the oxide, a tunneling current flows, which depends on the relative orientation of the magnetizations of the electrodes. An applied magnetic field can change the relative alignment causing a change in resistance. The so-called tunnel magnetoresistance, TMR, is a measure of the sensitivity to magnetic fields of the device.

The most successful junctions use an aluminum oxide tunneling barrier, which is made by oxidation of an ultrathin layer of aluminum. Several oxidation processes have been applied to obtain high quality Al₂O₃ barrier layers. Typically, natural oxidation (in a pure O₂ atmosphere) results in a lower TMR than plasma oxidized junctions. However, plasma oxidized junctions display a high specific resistance, resulting in a low signal-to-noise ratio of the device. Therefore, before plasma oxidized tunnel barriers are applicable, the specific resistance needs to be decreased. The work described in this thesis aims to obtain knowledge and understanding of the plasma oxidation process as a first step in gaining control of the process and improving the properties of ultra-thin plasma oxidized tunnel junctions.

In this research the main characterization tool has been a differential ellipsometer that has been adapted for in-situ use, with which real-time changes in the metallic layers of the tunnel junction can be measured during the oxidation process, with a resolution of a fraction of a monolayer.

First, we focussed on the dynamics of the oxidation process, neglecting the exact influence of the plasma for the moment. We established that the thermal oxidation process is described by the model of Cabrera, in which electrons tunnel towards adsorbed oxygen molecules, thereby setting up an electrical field across the oxide. Aluminum ions make a thermal hop (assisted by the field) from the Al/Al₂O₃ interface into the oxide, after which they
Abstract

are pulled across the oxide to the surface. There the Al ions react with oxygen and form new oxide. The rate is determined by the rate at which Al ions hop into the oxide, which is field dependent and therefore thickness dependent.

Furthermore, it is established that the grain-like morphology of the aluminum layer (which is induced by the sputtering process and the layers under the aluminum, and changes during the oxidation process) has a large influence on the exact oxidation behavior. We suggest that the field across the oxide is affected by the presence of the grains, and is dependent on the grain size and shape.

For the oxidation of the thinnest aluminum layers (0.4 to 0.7 nm), we observed, using the real-time ellipsometer, the oxidation time at which over-oxidation of the bottom electrode starts. This makes our ellipsometer technique potentially applicable for process control for low-resistance tunnel junctions.

Next, we focussed on the influence of the plasma. Oxidation dynamics studies in various plasma conditions (i.e. various plasma power, pressure) are combined with plasma characterization in order to develop a model of the plasma oxidation process. Langmuir probes, with which the conductivity of the plasma can be measured, have been used to measure the ion density and electron temperature. Two-photon Absorption Laser Induced Fluorescence (TALIF) has been applied to measure the density of atomic oxygen, and, via a dissociation scheme, simultaneously the density of ozone as well. We found that the signal of atomic oxygen was overwhelmed by the ozone signal; the O density was not measurable using TALIF in this plasma. About 10% of ozone was observed to be present in the plasma, and it remained in the oxidation chamber for several hours after the plasma was turned off due to a very low rate of dissociation. Using actinometry, the density of atomic oxygen was measured, and found to be present in relatively small quantities in the order of 1% of the total gas pressure.

Using these observations, a novel model is developed, involving both oxygen ions and atoms from the plasma to accelerate the oxidation process. In this model, oxygen ions can deliver very locally a large amount of energy to the sample (a ‘thermal spike’), increasing the temperature for a short time and assisting in the hop of aluminum ions into the oxide. The oxygen atoms from the plasma can increase the field over the oxide, thereby lowering the activation barrier for aluminum ions to hop into the oxide, accelerating the rate of oxidation. The rate is determined by the flux of ions from the plasma, and the oxidation rate as function of thickness depends now on the spread of the thermal energy delivered by the ion. Using the model to simulate the oxidation rate from the measured oxygen ion and atom densities, a good fit to the oxidation rates as measured with the ellipsometer was found,
supporting the validity of our model.

Using the theory of our model, we give suggestions explaining the difference in tunnel barrier properties of plasma oxidation with respect to thermal oxidation. The first difference lies in the large amount of energy delivered by the ions, rearranging the oxide into a more relaxed structure, and possibly driving out defects, impurities and pinholes. A second effect is the higher sensitivity of the plasma oxidation rate to small differences in oxide thickness as opposed to the thermal oxidation rate, resulting in a more homogeneous oxide thickness. This explains the higher specific resistance that is generally observed for plasma oxidized junctions.

In a separate project, Atomic Layer Deposition (ALD), a novel $\text{Al}_2\text{O}_3$ deposition technique, was investigated for applicability in MTJs. ALD is a chemical deposition process in which two gases react separately with the sample surface, theoretically depositing exactly one monolayer of a material per deposition cycle. Advantages are a theoretically perfect thickness control, a low pinhole density, and a perfect surface coverage. However, the complete process relies on a correct high-quality initial surface termination for the first reaction step. In MTJs, this was found to be difficult to achieve. We observed that the thickness control is far from perfect due to the first few layers, and the very reactive gases damage the bottom electrode, negatively influencing the TMR. Before ALD is applicable in MTJs, a combination of reaction gases needs to be found such that the bottom electrode is not damaged and the thickness control is improved.
Samenvatting

Zogenaamde ‘Magnetische tunnelstructuren’ (Magnetic tunnel junctions, MTJs) zijn elektrische componenten waarvan de elektrische weerstand zeer sterk verandert als een aangelegd magnetisch veld van richting verandert. Deze MTJ’s zijn toepasbaar als niet-fluchtig geheugenelement in het werkgeheugen van moderne computers, met als voordeel dat ze bijzonder energiezuinig zijn, en dat de computer willekeurig uit en aan gezet kan worden zonder dat de informatie in het geheugen verloren gaat.

Een magnetische tunnelstructuur bestaat uit twee ferromagnetische geleidende electrodes, gescheiden door een isolerend laagje (‘barrière’) met een dikte in de orde van een nanometer. Als een spanning aangelegd wordt over de electrodes, zal er een kleine tunnelstroom gaan lopen, waarvan de sterkte afhangt van de relatieve richtingen van de magnetisatie van de electrodes. De relatieve verandering in de weerstand ten gevolge van een extern magnetisch veld wordt de tunnelmagnetoweerstand (TMR) genoemd.

De barrière van de meeste succesvolle juncties is gemaakt van aluminiumoxide, dat meestal gemaakt wordt door een extreem dun laagje aluminium te oxideren. Het oxidatieproces kan op verschillende manieren worden verwezenlijkt. Oxidatie in puur zuurstof (natuurlijke oxidatie) resulteert in MTJ’s met een lagere TMR dan juncties gemaakt in een zuurstofplasma. Echter, op plasmaoxidatie gebaseerde juncties hebben ook een hogere specifieke weerstand, hetgeen de signaal-ruis-verhouding negatief beïnvloedt. De hoge oxidatiesnelheid maakt plasmaoxidatie een aantrekkelijk proces in de productie, maar voordat op plasmaoxidatie gebaseerde juncties toepasbaar zijn zal eerst de specifieke weerstand verlaagd moeten worden. Het werk beschreven in dit proefschrift heeft als doel het verkrijgen van kennis en begrip van het plasma oxidatieproces, om uiteindelijk het proces te kunnen beheersen en de eigenschappen van zeer dunne magnetische tunneljuncties te kunnen verbeteren.

Het belangrijkste instrument in dit onderzoek is een differentiële ellipsometer, die aangepast is voor in-situ gebruik, zodat tijdens het oxidatieproces, in real-time, kleine veranderingen (fracties van een monolaag) in de MTJ-structuur gevolgd kunnen worden.

We hebben gevonden dat het thermische oxidatieproces goed beschreven

Ook is vastgesteld dat de korrelstructuur van het aluminium van invloed is op het oxidatieproces: als de korrels kleiner zijn zal het veld in het oxide lager zijn, en dus zal ook de oxidatiesnelheid lager zijn. De exacte structuur van het aluminium wordt beïnvloed door het depositieproces, door de onderliggende lagen, en door het oxidatieproces zelf.

Voor toepassing in lage-weerstand MTJ’s worden barrières gemaakt van 0.4 tot 0.7 nm aluminium. We vinden dat we met behulp van de realtime ellipsometer het tijdstip waarop oxidatie van de onderelectrode begint kunnen bepalen. Dit maakt de ellipsometer mogelijk geschikt om toegepast te worden voor productiebeheersing van lage-weerstand tunnel juncties.

Het plasma-oxidatie-proces is in verschillende plasmacondities (plasma- vermogen, -druk, -afstand) bestudeerd, door de oxidatiesnelheid te meten en te vergelijken met eigenschappen van het plasma. Met een Langmuir sonde is de ionendichtheid en elektronentemperatuur gemeten. TALIF (Two-photon Absorption Laser Induced Fluorescence) is gebruikt om de dichtheid van atomair zuurstof (O) te meten, en simultaan, via een dissociatiestap, ook de ozon dichtheid te bepalen. We vonden dat de O-dichtheid lager is dan de $O_3$-dichtheid, waardoor de hoeveelheid O niet te meten is met TALIF. Ongeveer 10% ozon is gedetecteerd in het plasma, en door de lange levensduur van meer dan een uur blijft het ozon in de kamer achter als het plasma wordt uitgezet. Met behulp van actinometrie is vervolgens de dichtheid van atomair zuurstof bepaald.

Samenvatting

Berekeningen aan de hand van een erg simpel, macroscopisch model van de verspreiding van de thermische energie door de laag heen geven een kwalitatief redelijke overeenkomst met de metingen, maar simulaties van ion-inslag aan het oppervlak zouden een beter inzicht in het feitelijk proces kunnen geven.

Gebruikmakend van het model hebben we de oxidatiesnelheid berekend als functie van de gemeten dichtheid van ionen en atomen in het plasma, en dit vergeleken met de oxidatiesnelheid die gemeten is met de ellipsometer. Een erg goede fit is gevonden, hetgeen ons model ondersteunt.

Aan de hand van ons model geven we suggesties met betrekking tot de invloed van het plasma oxidatieproces op de eigenschappen van de tunneljunctie. Ten eerste kan de thermische piek van de inslag van een ion zorgen voor een andere structuur van het oxide, en mogelijk ook zorgen voor het verwijderen van onzuiverheden en ‘structuurfoutjes’ in het oxide. Ten tweede is de plasmaoxidatiesnelheid veel gevoeliger voor kleine variaties in oxide dikte, waardoor het oxide homogener van dikte is in vergelijking met natuurlijk geoxideerd aluminium. Dit zou de hogere weerstand van op plasmaoxidatie gebaseerde junctions kunnen verklaren.

In een apart project is onderzocht of Atomic Layer Deposition (ALD), een erg nieuwe depositie techniek, bruikbaar is om de aluminiumoxide tunnel barrière te maken. ALD is een chemisch depositie proces waarin twee precursors afwisselend reageren met het oppervlak en zo, per reactie-cyclus, exact één monolaag achterlaten. De voordelen van deze techniek zijn een theoretisch perfect controle over de dikte van de laag, een lage dichtheid van pinholes (geleidende paden door het oxide) en een perfecte oppervlakte-bedekking. In magnetische tunnelstructuren blijkt echter dat de groei niet goed beheerst wordt en dat de onder-electrode beschadigd wordt door de reactieve gassen die gebruikt worden. Voordat ALD toepasbaar is voor magnetische tunnel junctions, zal eerst een combinatie van precursors gevonden moeten worden die de onder-electrode niet beschadigen en een betere groei van de eerste lagen oplevert.
Curriculum Vitae

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Presentations

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Publications


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