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MASTER

Silicon surface passivation by thin films studied by corona charging

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Silicon surface passivation by thin films studied by corona charging

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Abstract

Surface passivation of $c$-Si by thin films is becoming of vital importance in photovoltaics, as solar cells experience an increasing surface-to-volume ratio due to the cost-driven reduction of cell thickness. Passivation of unsaturated Si bonds by e.g. atomic hydrogen is called chemical passivation. Surface passivation can also be achieved by shielding the minority charge carriers from the semiconductor interface by means of an internal electric field. This method is referred to as field-effect passivation.

In order to investigate field-effect passivation of silicon surfaces, the first part of this work is concerned with the construction and characterization of an experimental setup. This so called corona charger is used for the generation and deposition of corona charges on top of thin films deposited on $c$-Si wafers. During the setup characterization phase, the important aspects of the corona charging process have been identified and the setup has been optimized in terms of corona charge uniformity and corona charge deposition rate.

The corona charging technique is demonstrated by application to Al$_2$O$_3$ and SiN$_x$ films deposited onto $c$-Si wafers. It is shown that the fixed charge density, which induces the field-effect passivation properties of the film, can be measured by depositing corona charges with the opposite polarity. With the effect of field-effect passivation nullified, only chemical passivation properties of the film remain. It is shown that the surface passivation properties of Al$_2$O$_3$ outperform those of SiN$_x$. At corona charge densities beyond the fixed charge density (typically $-5.6\cdot10^{12}$ cm$^{-2}$ for Al$_2$O$_3$ and $2.9\cdot10^{12}$ cm$^{-2}$ for SiN$_x$), additional charge becomes trapped into the film, enabling the manipulation of the fixed charge density in the film.

It is also demonstrated that with an additionally deposited capping layer, corona charging can be performed on ultrathin films, as they suffer from dielectric breakdown without this additional layer. Corona charging experiments have been performed onto Al$_2$O$_3$ films synthesized by thermal atomic layer deposition (ALD), with thicknesses down to 5 nm for the Al$_2$O$_3$ layer. It is shown that in contrast to the 10 and 30 nm thick Al$_2$O$_3$ films, the chemical passivation properties go down for the 5 nm film, while the field-effect passivation properties are comparable for all three thicknesses.

Finally, the corona charging technique has been used in combination with second-harmonic generation (SHG), another diagnostic technique available in the group. SHG is sensitive to internal electric fields through the effect of electric-field-induced SHG (EFISH) and has the ability to indicate the presence of charge in a qualitative way. The corresponding fixed charge density, obtained by corona charging, can be used for quantification of the EFISH intensity. It is shown that the results obtained by corona charging are in good agreement with the analytical model which relates the EFISH intensity to a given charge density.
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1. Introduction

1.1 The projected future energy mix & photovoltaics

While fossil fuels are being exhausted at a high pace, global energy consumption continues to rise. Taking climate and geopolitical issues into account, it is imperative that a shift in thinking pattern will take place and that future developments will focus on renewable energy.

When looking into more detail at the projected future energy mix \cite{1}, as shown in Figure 1.1, it can be seen that several renewable energy sources are expected to become more important in the future. Traditional fossil fuels such as coal, oil and natural gas are not expected to be depleted by the year 2100, but their relative share in the future energy supply will decrease significantly. Renewable energy sources such as wind, biomass, water and solar energy are expected to dominate the energy supply in the future. Solar energy is expected to account for even more than 60% of the energy mix in the far future. Solar energy can be harvested in the form of heat and electricity.

![Figure 1.1: The future energy mix as projected by German Advisory Council on Global Change \cite{1}.

The last decade has seen photovoltaic (PV) technology emerging as a potentially major technology for global power generation. The continuous growth experienced in the last ten years is expected to continue in the coming years. By the end of 2008, the world cumulative PV power installed was approaching 16 GW \cite{2}, and today almost 23 GW is installed globally which produces about 25 TWh of electricity on a yearly basis \cite{2}. PV could provide up to 12% of the European electricity demand by 2020 and be competitive with other electricity sources in as much as 76% of the European electricity market by 2020 \cite{2}.
The photovoltaic effect was first discovered by Becquerel in 1839, demonstrating that electrons could interact with electromagnetic radiation\textsuperscript{[3]}. This interaction is the physical principle behind PV devices that convert sunlight into electricity. The first PV devices based on crystalline silicon (c-Si) with reasonable conversion efficiency were demonstrated by Chapin et al. at AT&T Bell labs in 1954 \textsuperscript{[4]}. This c-Si solar cell demonstrated an energy conversion efficiency of \~6 \% \textsuperscript{[4]}, and in recent years the record efficiency has been increased up to 24.7 \% \textsuperscript{[5]}. Wafer-based silicon solar cells are still the main technology with a market share of 80 \% in 2009 and have typical commercial module efficiencies of 12 - 20 \% \textsuperscript{[2]}.

1.2 The c-Si solar cell

In this section the basic principle of a c-Si solar cell will be discussed. The most commonly used c-Si solar cells are large area p-n junctions made from silicon. Where p-type c-Si is typically boron doped, n-type c-Si is typically phosphorous doped. Figure 1.2 schematically illustrates an advanced n-type based c-Si solar cell design.

When a photon hits the c-Si solar cell, three events can take place:

- The photon gets reflected of the surface.
- The photon passes straight through the cell and is not absorbed.
- The photon gets absorbed by the silicon and generates an electron-hole pair.

In case of the first two events, the photon energy is lost. Low energy photons usually pass straight through the silicon, since the band gap energy of silicon (1.12 eV) is larger than the energy of the photons. Therefore these photons cannot be absorbed by the material and do not contribute to the electrical output. If the energy of the photon is equal to, or higher than the band gap, there is a much bigger chance of absorption which results in the creation of an electron-hole pair. Excess energy of the photons is lost as heat.

To make optimal use of the incoming light, the front of the cell has a textured surface, which scatters the incoming light, thereby enlarging the optical path length of the photons through the active layer and improving the chance of a photon being absorbed. In combination with an anti-reflection coating more light can be captured and directed into the c-Si. A back reflector is used to reflect the light back into the active layer, giving
photons an extra chance to generate charge carriers. A part of the generated charge carriers is lost due to recombination in the bulk of the c-Si wafer and at the front and back surface of c-Si. The surface recombination losses can be reduced by the application of a functional thin film, a so called passivation layer. The importance of this passivation layer, basically the topic of this work, will be addressed in Section 1.4.

1.3 Loss mechanisms in a c-Si solar cell

Defined in 1961, the Shockley-Queisser limit established that a single-junction solar cell without sunlight concentration (operating at “one sun”) has a maximum theoretical efficiency of about 31% [6]. After correcting for inherent losses, as illustrated in Figure 1.3, this usually translates into efficiencies of ~15% for commercially available c-Si solar cells.

![Diagram of loss mechanisms in a c-Si solar cell]

**Figure 1.3:** Schematic of the various loss mechanisms which contribute to the reduction in efficiency of a typical c-Si solar cell.

The difference between this theoretical maximum and the efficiencies that modern c-Si solar cells reach in practice is mainly due to practical issues, such as reflection losses at the front of the solar cell and light blockage caused by the electrical contacts. The major loss, the spectral mismatch, is due to the fact that more than half of the available sunlight has an energy less than 1.12 eV and cannot be converted into electricity directly. The recombination losses of charge carriers at the c-Si surface however, can be reduced by surface passivation. Surface passivation of c-Si is becoming of vital importance in PV, as solar cells experience an increasing surface-to-volume ratio due to the cost-driven reduction of the cell thickness. Consequently, an excellent level of surface passivation is a requisite for high efficiency c-Si solar cells. This work will focus especially on surface passivation of c-Si by thin films and in the next section surface passivation will be addressed in more detail.
1.4 Surface passivation

As concluded in Section 1.3, surface passivation of c-Si is very important for the performance of high efficiency solar cells. An excellent electrical interface quality is essential for exploiting the optimal electronic properties of the c-Si bulk. The surface of c-Si can be considered as a severe interruption from its crystallographic structure. This gives rise to energy levels in the otherwise forbidden band gap, which can be effective recombination centers for charge carriers. To reduce these recombination losses, passivation of the interface is required. The recombination rate depends on the interface defect density, so the first strategy is to reduce the number of defect states at the semiconductor surface. The surface defect density can be lowered by passivation of unsaturated Si bonds (dangling bonds) by e.g. atomic hydrogen. This passivation method is called chemical passivation. Passivation can also be achieved by shielding the minority carriers from the semiconductor interface by means of an internal electric field. This second passivation method is referred to as field-effect passivation. Field-effect passivation dramatically decreases the electron or hole concentration close to the c-Si surface, and consequently, the surface recombination losses are significantly reduced. Both passivation mechanisms are schematically illustrated in Figure 1.4.

![Figure 1.4: Schematic representation of the surface passivation mechanisms. The electrons and defects are represented by the red dots and black spots respectively. In situation (a) the c-Si surface is not passivated at all and a rather large amount of defects is present. Situation (b) illustrates the chemical passivation mechanism, as the amount of defects is dramatically decreased. In situation (c) field-effect passivation is illustrated, where an internal electric field induced by the negative fixed charges in Al$_2$O$_3$ acts as a barrier to prevent the electrons from reaching the surface. In situation (d) both passivation mechanisms are present resulting in the best possible surface passivation.](image-url)
1.5 Atomic layer deposition

Within the Plasma & Materials Processing (PMP) group at the Eindhoven University of Technology, it has been demonstrated by Hoex et al. that thin layers of Al₂O₃ provide an excellent level of silicon surface passivation [7]. Atomic layer deposition (ALD) is an advanced technique for depositing metal oxide thin films and has been used throughout this work for depositing Al₂O₃ films. On the virtue of two separate self-limiting surface reactions, ALD has the ability to control film growth and material properties on the atomic level. The principle of ALD is illustrated in Figure 1.5.

Figure 1.5: Schematic illustration of ALD. The most common ALD process uses H₂O during the oxidation half-cycle. Also other oxidation sources can be employed such as an O₂ or O₃ plasma. When an O₂ plasma is used, the method is referred to as plasma assisted ALD, as opposed to thermal ALD when H₂O or O₃ are employed.

The two half-reactions consist of an Al(CH₃)₃ (also known as trimethylaluminum or TMA) dosing step and an oxidation step. The first half-cycle consists of self-limiting reaction of TMA molecules with the surface groups available (OH) and a purge step to remove the volatile reaction by-products and the excess of precursor dosed. After this first half-cycle, a sub-monolayer of precursor has chemisorbed on the surface. During the second self-limiting surface reaction, the surface is exposed to reactant molecules (H₂O
for thermal ALD and an O$_2$ for plasma assisted ALD) which react with the surface groups (CH$_3$) of the adsorbed precursor. The second half-cycle is completed by another purge step to remove the volatile reaction by-products and the excess of reactant dosed. After the full ALD cycle, a sub-monolayer of material is deposited and the surface groups are again similar to the start of the cycle. Subsequently, the cycle can be repeated to deposit a film with the thickness targeted.

In addition to thermal and plasma assisted ALD, also plasma enhanced chemical vapor deposition (PECVD) is used for the deposition of thin films. The PECVD process is used for depositing thin films from a gas state to a solid state onto a substrate, by chemical reactions occurring after the creation of a plasma from the reacting gasses.

1.6 Goal of this work

The work presented in this thesis can be divided into three parts. The goal of the first part was to construct and implement a new setup to investigate the passivation properties of thin films, a so called corona charger. Parameters that play an important role during the corona charging process had to be identified. After getting the corona charger up and running, a part of this work focused on further improving the setup in terms of charge distribution, charge uniformity and charge deposition speed onto the sample.

In the second part of this work, the corona charger is used to investigate the surface passivation of c-Si by thin films. Corona charging can be used to quantify the intrinsic fixed charge density in thin films, responsible for field-effect passivation. It is shown that corona charging allows for differentiation between chemical and field-effect passivation, so the main passivation mechanism can be identified. In this work, two different films are investigated: Al$_2$O$_3$ synthesized by thermal ALD, plasma ALD and PECVD, and SiNx grown by PECVD.

In the third part of this work, corona charging is also used for investigating other physical phenomena. Issues addressed in this thesis are:

- The manipulation of the fixed charge density of Al$_2$O$_3$ and SiNx films, by trapping and de-trapping charge into the film by depositing corona charges on top of the sample.
- The investigation of a thickness dependence of the passivation properties of Al$_2$O$_3$, as it has been shown that the passivation quality decreases for ultrathin films [8].
- Whereas corona charging can be used to investigate field-effect passivation in a quantitative way, second-harmonic generation (SHG) has the ability to indicate field-effect passivation in a qualitative way, due to the sensitivity to internal electric fields. As both diagnostics are complementary, a relation between them enables for extracting the fixed charge density from the SHG data directly.

1.7 Outline of this thesis

This thesis contains 5 chapters and is structured as follows. In Chapter 2 the experimental background and theoretical aspects of the corona charging are discussed. The physical principles behind the corona charger and the Kelvin probe and the influence of surface
and/or oxide charges on surface potential measurements are also addressed in this chapter. Chapter 3 describes the part of this work that focused on the construction and characterization of the corona charging setup. The investigation of the corona charging parameters and the implemented improvements are described, together with the measurement procedure. Chapter 4 shows and discusses the results of the experiments performed and finally, in Chapter 5, the main conclusions and recommendations are presented.
2. Experimental & theoretical aspects

2.1 Sample fabrication & minority carrier lifetime

2.1.1 Sample fabrication

Intrinsic charges in thin films are very important for device applications. One example is the presence of these charges in thin films employed for surface passivation of c-Si solar cells, where the fixed charges provide field-effect passivation \[^9\]. To understand the corona charging principle, it is necessary to give a short description of sample fabrication first. The process starts with the preparation of c-Si wafers. Throughout this work, mostly double-side polished low resistivity (3.5 \(\Omega\) cm) n-type float zone c-Si wafers with a thickness of 275 \(\mu\)m have been used. Prior to deposition the c-Si wafers received an HF dip to remove the native oxide. Identical films of Al\(_2\)O\(_3\) (usually 30 nm thick) are then deposited on both sides of the c-Si wafer as shown in Figure 2.1. An interfacial SiO\(_x\) layer with a thickness of ~1.5 nm is formed unintentionally between the c-Si and Al\(_2\)O\(_3\) as a result of the deposition process \[^{10}\], and the combination of the Si and Al\(_2\)O\(_3\) material systems.

![Figure 2.1](image1.png)

**Figure 2.1:** Schematic representation of a c-Si wafer with identical films of Al\(_2\)O\(_3\) deposited on both sides. Between the Al\(_2\)O\(_3\) and c-Si wafer an interfacial SiO\(_x\) layer of ~1.5 nm is present. The dimensions are not to scale.

After the deposition of Al\(_2\)O\(_3\), the wafer receives an anneal treatment. A typical anneal treatment is performed at 400 °C in a N\(_2\) atmosphere for 10 minutes. During this annealing process, the negative fixed charge density increases at the Al\(_2\)O\(_3\) – SiO\(_x\) interface \[^{11}\], as schematically illustrated in Figure 2.2.

![Figure 2.2](image2.png)

**Figure 2.2:** Schematic illustration of the negative fixed charge density at the Al\(_2\)O\(_3\) – SiO\(_x\) interface. Due to the negative fixed charge density, electrons in the c-Si bulk are repelled from the interface and a positively charged space-charge region is induced at the c-Si interface (shown for the top-surface only).
The presence of these negative fixed charges provides field-effect passivation. Electrons in the c-Si bulk are repelled from the interface, reducing recombination losses and enhancing the efficiency of a c-Si solar cell.

### 2.1.2 Minority carrier lifetime

The combined electronic losses in the c-Si bulk and the c-Si surfaces result in a so-called effective lifetime $\tau_{\text{eff}}$ of the photo-excited charge carriers in a c-Si wafer. The standard technique to determine this effective lifetime of the minority charge carriers is the photoconductance technique developed at Stanford University and commercialized by Sinton Consulting\cite{12}. In first approximation $\tau_{\text{eff}}$ of a symmetrically passivated c-Si wafer can be expressed as \cite{13}:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surface}}} + \frac{2S_{\text{eff}}}{d} \tag{2.1}$$

where:

- $\tau_{\text{bulk}}$ is the bulk lifetime,
- $\tau_{\text{surface}}$ is the surface lifetime,
- $d$ is the thickness of the c-Si wafer,
- $S_{\text{eff}}$ is the effective surface recombination velocity.

Wafers of c-Si with a high bulk lifetime are commercially available, and consequently, $\tau_{\text{eff}}$ is dominated by recombination losses at the c-Si surfaces. In this case, the bulk lifetime is assumed to be infinite, and the upper limit of the surface recombination velocity (SRV) is given by:

$$S_{\text{eff, max}} \approx \frac{d}{2} \frac{1}{\tau_{\text{eff}}} \tag{2.2}$$

The lifetime can be measured with the Sinton lifetime tester. In operation, a light flash shortly illuminates the wafer and excess charge carriers are generated. By simultaneously monitoring the photoconductance and light intensity, the effective lifetime can be determined as a function of the excess carrier density (i.e. injection level) \cite{13}. A drawback of the photoconductance technique is its relatively large detection area of ~6 cm$^2$, and consequently no spatially resolved information can be obtained.

### 2.2 The corona charging principle

A powerful method to investigate field-effect passivation is corona charging. Figure 2.3 shows a schematic representation of a setup for the generation and deposition of corona charges. The c-Si wafer, symmetrically coated by a thin film (see Figure 2.2) is placed on a grounded metal plate. A tungsten needle is located ~10 cm above the sample. At the tip of the needle, a high voltage in the range of 5-10 kV is applied. A high electric field is
generated and causes the surrounding air molecules to ionize. Depending on the polarity of the applied voltage, positive or negative corona charges can be generated. Ninety percent of the negative charges consist of $\text{CO}_3^-$ ions, whereas for positive charging the main part of the charges consist of hydrated $\text{H}_3\text{O}^+$ ions and, additionally, of $\text{NO}^+$ and $\text{NO}_2^+$ ions for high humidity conditions. A stainless steel grid is placed above the wafer and is kept at a fixed voltage. The grid is necessary for improving the distribution of corona charges over the sample surface, thereby increasing the charging uniformity.

One of the goals of this project is to quantify the intrinsic fixed charge density in thin films. Corona charging works on the principle of compensating the effects of the intrinsic fixed charge. In case of $\text{Al}_2\text{O}_3$ films, the polarity of the corona charger is set to produce positive corona charges. When deposited on the $\text{Al}_2\text{O}_3$, these positive corona charges will counter the effect of the negative fixed charges in the annealed $\text{Al}_2\text{O}_3$ film. The field-effect passivation properties will decrease and the electrons in the $c$-Si can reach the silicon interface with less difficulty (shown in Figure 2.4) resulting in increased recombination losses. When all the negative fixed charges at the $\text{Al}_2\text{O}_3 - c$-Si are compensated by positive corona charges on top of the sample, the field-effect passivation

**Figure 2.3:** Schematic representation of the setup constructed for the generation and deposition of corona charges. In the particular case shown positive corona charges are generated.
mechanism is completely nullified and the remaining passivation mechanism is of chemical nature.

Figure 2.4: Schematic representation of the corona charging process. The positive corona charges on top of the sample will counter the effect of the negative fixed charges in the annealed Al₂O₃ film, allowing electrons in the c-Si to reach the silicon interface with less difficulty.

When even more positive corona charges are deposited on top of the Al₂O₃ layer, the field-effect passivation will increase again, but is now induced by a net positive charge density caused by the excess of corona charges. The difference is that now the positive charge carriers in the c-Si bulk are repelled from the interface instead of the electrons. A maximum value for the SRV will therefore be observed at the “compensation point” where the field-effect is nullified.

2.3 The Trek 325 electrostatic voltmeter

Once corona charges have been deposited on a sample, a device is needed to determine the amount of deposited corona charges. The Trek 325 electrostatic voltmeter is based on a vibrating capacitive probe and is a useful tool for measuring surface charge or surface potentials. An advantage of capacitive probe measurements is that it allows for non-
contact and non-destructive examination of the surface charge or potentials. The device has therefore been used for that purpose during this project. Its principle of operation is explained in this section.

2.3.1 The capacitive probe

The technique of capacitive probe measurements is based on the experimental approach of Lord Kelvin \cite{17} and the principle of operation has its origin in the equation of the capacitance of a capacitor:

\[ C = \frac{Q}{U} \tag{2.3} \]

Where:

- \( C \) is the capacitance of a capacitor,
- \( Q \) is the charge accumulated by the capacitor,
- \( U \) is the potential difference between the plates of the capacitor.

A capacitor in its most simple form consists of two parallel conductive plates. The capacitance depends on the surface area \( A \) of the plates and the distance \( d \) between the plates. The capacitance of this parallel-plate capacitor can be expressed as:

\[ C = \frac{\varepsilon_r \varepsilon_0 A}{d} \tag{2.4} \]

Where:

- \( \varepsilon_r \) is the relative electric permittivity of the medium between the capacitor plates,
- \( \varepsilon_0 \) is the electric permittivity of vacuum \((8.85 \cdot 10^{-12} \text{ F/m})\),

The capacitive probe is based on the same configuration as a parallel-plate capacitor. The capacitor is now formed by the sample and the probe itself, as shown in Figure 2.5.

\[ \text{Figure 2.5: The parallel-plate capacitor.} \]
The voltage $U_1$ corresponds to the potential difference between the probe and the ground and $U_2$ corresponds to the potential difference between the sample and the ground. The voltage $U$ between the probe and the sample is then equal to $|U_1 - U_2|$. If in this case the probe is grounded, then $U_1 = 0$ and $U = U_2$. The charge $Q$ on the sample can then be calculated:

$$Q = U \frac{\varepsilon_r \varepsilon_0 A}{d}$$  \hspace{1cm} (2.5)$$

As long as $U$ can be determined, the charge on the sample can be calculated. The disadvantage of the capacitive probe is that it is a rather slow method for determining surface charge or surface potentials. A measurement method based on a vibrating capacitive probe is faster in operation and is more commonly used for these measurements.

**2.3.2 The vibrating capacitive probe**

If the distance $d$ is modulated in time, as illustrated in Figure 2.6, the voltage between the probe and the test surface will also vary. In order to keep $U$ constant, it is necessary to adjust $U_1$ accordingly, since $U_2$ is constant. This means that electric charge is added to or removed from the probe.

![Figure 2.6: The vibrating capacitive probe.](image)

This leads to the principle of the Kelvin probe. A change in distance between the probe and the sample during time interval $dt$ requires a change in electric charge $dQ$, in order to keep $U$ constant. The distance $d$ from Figure 2.5 can be expressed as:

$$d(t) = d_0 + d_1(t)$$ \hspace{1cm} (2.6)$$

as shown in Figure 2.6, where:

- $d_0$ is a constant distance between the probe and test surface,
- $d_1(t)$ is a change in distance between the probe and test surface over time.

When equation (2.5) and (2.6) are combined, equation (2.5) leads to:
Equation (2.7) can be differentiated to time, which leads to:

\[
\frac{dQ}{dt} = -U \frac{\varepsilon_r \varepsilon_0 A}{d_0 + d_1(t)} \cdot \frac{d(d_1(t))}{dt}
\] (2.8)

The expression \(dQ/dt\) represents an electric current \(I\), which is flowing either from or towards the probe. A change in distance of the probe also causes a change in current. A method based on this change in current can be used to determine the surface potential and/or charge and is called the null method. In the null method, an external voltage \(U_1\) is applied to the probe. This voltage is adjustable in order to bring the potential difference \(U\) to the desired value. If \(U_1\) equals \(U_2\), the voltage \(U\) will be zero and no current will flow towards or from the probe. In other words, whenever during the movement of the probe the current becomes zero, the potential of the probe is equal to the potential of the sample. The charge can then be calculated according to equation (2.5).

### 2.3.3 The Kelvin probe principle

The Trek 325 electrostatic voltmeter is based on the Kelvin probe principle. The Kelvin probe vibrates perpendicular to the test surface and the current flowing towards or from the probe changes proportionally to the amplitude and frequency of the vibration. For a sinusoidal motion of the probe, equation (2.6) yields:

\[d(t) = d_0 + d_2 \sin(\omega t)\] (2.9)

Where:

- \(d_2\) is the amplitude of the vibration,
- \(\omega\) is the angular frequency, where \(\omega = 2\pi f\) with \(f\) the frequency of the vibration.

According to equation (2.4), the capacitance is then given by:

\[C = \frac{\varepsilon_r \varepsilon_0 A}{d_0 + d_2 \sin(\omega t)}\] (2.10)

And the current is then according to equation (2.8):

\[I = \frac{dQ}{dt} = -U \frac{\varepsilon_r \varepsilon_0 A}{(d_0 + d_2 \sin(\omega t))^3} \cdot d_2 \omega \cos(\omega t)\] (2.11)
To nullify this current, the voltage $U$ has to be brought to zero. Only then will the probe-to-ground voltage $U_1$ be equal to the voltage on the surface $U_2$. From this surface voltage, the charge can be calculated according to equation (2.5).

### 2.3.4 Limitations of the Kelvin probe

There are some factors that could influence the sensitivity and accuracy of the Kelvin probe.

- **Noise**
  The Kelvin probe can be very sensitive to electromagnetic and mechanical noises. During the measurement the current is being nullified due to changes in the probe-to-surface distance. When that minimum is reached, the signal-to-noise ratio is also at its minimum. At this moment noise can cause a significant offset in the detected current. Noise problems can be partially avoided by employing proper filtering and shielding techniques.

- **Stray capacitance**
  A capacitive probe does not only respond to the test surface, but also to all distributed capacitances in the surrounding environment. These additional capacitances are also being modulated during the movement of the vibrating probe. These effects can be avoided by appropriate shielding.

- **Spacing problems**
  The voltage $U_1$ applied to the probe in order to nullify the current should be independent of the geometry of the probe. In practice however, it could vary due to:
  - Non-parallel probe and test surface.
  - Edge effects and a non-homogeneous electrical field between the probe and the test surface.
  - Capacitive coupling.
  - Non uniform charge distribution on the test surface.

### 2.4 Surface charge

The surface voltage measured by a device based on the Kelvin probe principle is usually the result of surface or insulator charge and/or the work function difference between the sample and the probe. In case of the Trek 325 electrostatic voltmeter, the probe is located typically 0.2 – 2 mm above the surface. The energy band diagram is therefore comparable with that of a metal-oxide-semiconductor (MOS) capacitor, except with the insulator replaced by air. The energy or potential diagram of the probe-air-semiconductor is schematically illustrated in Figure 2.7(a). Potentials are more appropriate than energy, because it is the potential that is measured. $W_M$ and $W_S$ represent the work function potentials of the metal and semiconductor respectively and are the potential difference between the vacuum potential $E_{\text{vac}}/q$ and the Fermi potential $\Phi_F$. $E_c/q$ and $E_v/q$ are the conduction and valence band potentials and $\Phi$ represents the intrinsic energy band
potential. The potential at the semiconductor surface $\Phi_S$ is zero for flatband, negative for accumulation and positive for depletion and inversion.

![Figure 2.7: The band diagram of a metal-air-semiconductor with no workfunction difference between metal and semiconductor: (a) without surface charge; (b) with surface charge.](image)

First consider the bare p-type semiconductor, as illustrated in Figure 2.7(a) with the probe at distance $d_{air}$ above the sample. The detecting probe is a Kelvin probe, so the external nulling voltage ensures that there is no probe current or charge. With no surface charge present at the semiconductor surface and with equal work functions $W_M$ and $W_S$, this leads to a work function difference of $W_{MS} = W_M - W_S = 0$. In the next situation, illustrated in Figure 2.7(b), a positive charge density $Q$ is deposited on the semiconductor surface, inducing a negative charge density $Q_i$ in the semiconductor. This charge density is induced in the semiconductor only, as the nulling voltage ensures that no charge builds up in the probe. Therefore no electric field is present between the sample and the probe, making $V_P = \Phi_S$.

Thin oxide films deposited on the semiconductor can contain charges and have work function differences. In order to better illustrate the effect of work function differences and charge density, a MOS capacitor is considered first. Figure 2.8 illustrates a MOS capacitor with a work function difference, a charge density $\rho_{ox}$ in the oxide and a charge sheet $Q_I$ at $x = x_I$. The gate voltage $V_G$ is given by:

$$V_G = V_{FB} + V_{ox} + \Phi_S$$  \hspace{1cm} (2.12)

Where $V_{ox}$ is the potential across the oxide and $V_{FB}$ the flatband voltage is given by:
\[ V_{FB} = W_{MS} - \frac{x_1}{d_{ox}} Q_1 - \frac{1}{C_{ox}} \int_0^{d_{ox}} \frac{x}{d_{ox}} \rho_{ox} dx \] \hspace{1cm} (2.13)

\[
\begin{array}{c}
0 \quad x_1 \quad d_{ox} \\
\end{array}
\]

\[ V_{ox} \]

\[ V_G \]

\[ Q_1 \]

\[ \rho_{ox} \]

Figure 2.8: (a) MOS capacitor with a charge density \( \rho_{ox} \) and a charge sheet at \( x = x_1 \); (b) The band diagram of the MOS capacitor.

In Figure 2.9(a) this is extended again towards the case where a Kelvin probe is held above a semiconductor covered with an insulator with a probe – semiconductor work function difference \( W_{MS} \). The work function difference leads to a negative probe potential \( V_p \). In Figure 2.9(b), also the oxide charge density \( \rho_{ox} \) and the surface charge density \( Q \) is considered. The probe voltage can now be calculated in the same way as for the MOS capacitor:\[19]\:

\[ V_p = V_{FB} + V_{air} + V_{ox} + \phi \] \hspace{1cm} (2.14)

Where the flatband voltage \( V_{FB} \) is now given by:

\[ V_{FB} = W_{MS} - \frac{d_{air}}{d} \frac{Q}{C} - \frac{1}{C} \int d_{air} \frac{x}{d_{air}} \rho_{ox} dx \] \hspace{1cm} (2.15)

Where \( C \) and \( d \) are respectively given by:

\[ C = \frac{C_{air} C_{ox}}{C_{air} + C_{ox}} \] \hspace{1cm} (2.16)

\[ d = d_{air} + \frac{d_{ox}}{\varepsilon_{ox}} \] \hspace{1cm} (2.17)

Equations (2.14) – (2.17) give the probe voltage due to \( W_{MS}, Q \) and \( \rho_{ox} \). The potential measured by the Kelvin probe is thus the sum of these individual contributions. The Kelvin probe is unable to distinguish between them during a measurement. In case of surface potential measurements during actual corona charging experiments, the corona
charge density $Q$ required to nullify the fixed charge density becomes sufficiently high to be able to neglect the influence of the other contributions to the probe voltage.

**Figure 2.9:** Band diagram for a probe-air-oxide-semiconductor with a work function difference; (a) with no charges (b) with surface charge and oxide charge (the black dots represent electrons).
3. Experimental setup & characterization

3.1 The experimental setups

Corona charging allows for the investigation of the fixed charge density in thin films. The corona charging procedure is based on the repetitive use of three experimental setups, as schematically illustrated in Figure 3.1.

The first setup, the corona charger, is used for the generation and deposition of corona charges on the sample surface. The deposited corona charges can counteract the field-effect passivation, induced by the interfacial fixed charge density, as described in Section 2.2. The second setup, the Trek 325 electrostatic voltmeter, allows for surface potential measurements in order to determine the deposited corona charge density on top of the sample. To complete one cycle of the measurement procedure, the charge carrier lifetime is determined with the Sinton lifetime tester. The carrier lifetime is a measure for the remaining level of surface passivation of the sample after each corona charging step. By repeating this cycle over and over again for different corona charge densities, field-effect passivation can be further counteracted and even be completely nullified for a certain corona charge density. At the moment the field-effect passivation has been completely nullified, the deposited corona charge density equals the fixed charge density in the passivating film.

The first goal of this project was to construct a corona charging setup. With the Sinton lifetime tester already available in the group, this means that an experimental setup for the corona charger and the Trek 325 electrostatic voltmeter had to be developed and constructed. As the physical principle of corona charging is already addressed in Chapter 2, this section gives an overview of the constructed setups and lists the components used. Figure 3.2 shows the corona charger and its components as constructed during this work.
Figure 3.2: The corona charger as constructed during this work.

1. The low voltage power supply is adjustable between 0-50 V. This power supply is connected to the stainless steel grid in order to keep it at a fixed potential. Usually this power supply is set to ± 10 V.

2. The high voltage power supply is adjustable between ± (0-10) kV. This power supply is connected to the needle of the corona charger in order to apply a high voltage on the corona needle. Usually this power supply operates at ± 9 kV.

3. This current meter monitors the corona current, giving an indication whether or not corona charges are being deposited. Usually this current is in the range of a few µA.

4. The corona charger as constructed during this work. It is surrounded by an acrylic box as a protection for the high voltages applied to the tip of the corona needle.

5. The stainless steel grid is important for the uniformity of deposited corona charge density on top of the sample. Section 3.2.1 discusses the aspect of uniformity of the deposited corona charge density in further detail. The height of the grid can be adjusted in steps of 0.5 cm with a maximum of 5 cm above the surface of the sample.

6. The grounded metal base plate. Samples are placed on top of this metal base plate and are positioned with the corona needle above their center.
The corona needle is the key component of the corona charger as it is used for the generation of corona charges. The tip of the needle has to be sufficiently sharp for the corona charge generation process to take place.

Figure 3.3 shows the setup constructed for the surface potential measurements during this work. The setup allows for accurate movement of the Kelvin probe above the sample in the x, y and z-direction.

**Figure 3.3:** *The Trek electrostatic voltmeter as constructed during this work.*

1. The position display unit, indicating the x, y and z-position of the Kelvin probe above a sample.
2. The control unit from the Trek 325 electrostatic voltmeter. This unit allows for the calibration prior to the measurements and also displays the surface voltage (the surface potential difference between the sample and the probe) measured by the Kelvin probe. See appendix A for an overview of the specifications of the Trek model 325.
3. The setup as constructed during this work for moving the Kelvin probe above a sample. A full rotation of the control wheels results in a horizontal or vertical displacement of 4 mm for the Kelvin probe.
4. The grounded metal base plate. Samples are placed on top of this metal base plate during the surface potential measurements.
5. Close up from the Kelvin probe. The probe can be moved in the x, y and z-direction with an accuracy of ±0.01 mm.
3.2 Characterization of the corona charging process

For corona charging two aspects are particularly important. The first aspect, the uniformity of the deposited corona charge density on top of a sample, is necessary for accurate surface potential measurements. The second aspect is the corona charge deposition rate, as corona charging can be quite a time consuming process. In the next two sections these aspects are investigated in order to control or enhance them.

3.2.1 The uniformity of deposited corona charge

During this work, corona charging experiments have been mostly performed on full 4-inch (10 cm) wafers. These wafers have a circular shape and the center of the wafer is positioned under the needle of the corona charger. The deposited charge distribution is also circular in shape with a maximum right under the needle and a minimum at the outer edges of the wafer. In the plot from Figure 3.4 the deposited charge distribution on top of a wafer is illustrated. The middle circular spot indicates the surface potential caused by the deposited corona charge distribution within 80-100 % of the maximum value. The ‘rings’ around this middle spot indicate the next intervals in steps of 20 %, all the way down to the lowest interval where the charge distribution is only within 0-20 % of the maximum value. Compared to the 10 cm diameter of a full wafer, the uniformity of the deposited charge is rather poor, as the middle spot is only ~4 cm<sup>2</sup> in size.

![Figure 3.4: The distribution of corona charges on top of the wafer.](image)

For optimal surface potential and lifetime measurements it is necessary to increase the uniformity of deposited corona charges. This can be achieved by adding a stainless steel grid to the setup and keeping it at a fixed potential. Instead of hitting the wafer directly, the corona charges now reach the grid first, resulting in a better charge distribution over the wafer. This effect is illustrated in Figure 3.5. The plot in Figure 3.5(b) shows the corona charge uniformity with the grid implemented into the setup at a bias voltage of 10 V. As a comparison, the plot in Figure 3.5(a) shows the uniformity of corona charges with the grid implemented, but without a bias voltage. Without a bias voltage, there is no
effect, as the uniformity does not increase and the middle spot still has a surface area of \(~4 \text{ cm}^2\). With the bias voltage applied, the uniformity of deposited corona charge does increase, as the center spot now covers \(~9 \text{ cm}^2\). The power supply connected to the grid can deliver a voltage in range of \(+ (0-50) \text{ V}\). The bias voltage has therefore been varied throughout this range in steps of 10 V, all giving the same result with the middle spot surface of \(~9 \text{ cm}^2\). The bias voltage is therefore kept at 10 V throughout all the measurements.

Figure 3.5: The deposited corona charge distribution on the surface of the wafer: (a) without a grid; (b) with a grid implemented into the corona setup.

Because the implementation of the grid had quite a significant effect on the uniformity of corona charges, the grid size has also been varied. Figure 3.6 includes a table with the specifications of the grid sizes used.

<table>
<thead>
<tr>
<th>Grid #</th>
<th>Grid wire thickness [mm]</th>
<th>Grid wire spacing [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.20</td>
<td>5.15</td>
</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td>2.48</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>1.061</td>
</tr>
<tr>
<td>4</td>
<td>0.22</td>
<td>0.415</td>
</tr>
</tbody>
</table>

Figure 3.6: The specifications of the different grids used for the improvement of the uniformity of deposited corona charges on a sample.

Grid number 1, 2 and 4 showed similar charge distribution plots as illustrated in Figure 3.5(b), with a center spot covering \(~9 \text{ cm}^2\). Grid number 3 however, consistently showed
charge distributions with a center spot covering up to \(~12 \text{ cm}^2\) as illustrated in Figure 3.7(b). Figure 3.7(a) is the same plot as Figure 3.5(b) and is added for comparison reasons.

**Figure 3.7:** The deposited corona charge uniformity is even further enhanced by using an optimal grid size.

The position of the grid above the sample has also been investigated in order to determine if this also contributes to the uniformity of deposited corona charge on the wafer. Figure 3.8 schematically illustrates the positions of the grid used for this experiment. The corona needle to base plate distance was kept constant during these measurements.

**Figure 3.8:** Schematic illustration of the grid position above the wafer in order to investigate the effect on the uniformity of the deposited corona charge.
Figure 3.9(b) shows the corona charge uniformity plot with the grid placed in the top position. The plot in Figure 3.7(b) was made with the grid in the middle position and is used again in Figure 3.9(a) for comparison reasons. With the grid placed in the top position, the middle spot surface increased in size up to ~18 cm$^2$, indicating even higher levels of corona charge uniformity on the wafer.

![Figure 3.9: The uniformity of deposited corona charges with the stainless steel grid: (a) in the middle position; (b) in the top position (for an illustration of the grid positions see Figure 3.8).](image)

The total progress in terms of charge uniformity achieved during this work. The plot in Figure 3.10(a) is at the very beginning of this project, while Figure 3.10(b) shows the charge uniformity in optimal configuration. The surface area of the middle spot, indicating the uniformity, increased from ~4 cm$^2$ up to ~18 cm$^2$ in the optimal configuration.

![Figure 3.10: The uniformity of deposited corona charges on a wafer: (a) uniformity at the very beginning of this project; (b) uniformity in the optimal configuration as used for the experiments.](image)
3.2.2 The corona charge deposition rate

The second important aspect, the corona charge deposition rate, has also been investigated. During actual measurements, it is important to control and keep track of the amount of deposited corona charges over time. The high voltage power supply has a range of ± (0-10) kV and Figure 3.11 illustrates the corona charge deposition rates at 7, 8 and 9 kV. In general higher voltages lead to an increased generation of corona charges at the tip of the corona needle, and consequently, a higher corona charge deposition rate. As expected, the deposition rate at 8 kV is higher than the deposition rate at 7 kV, but a significant increase could only be realized when this voltage was set to 9 kV.

![Corona charge deposition rate graph](image)

**Figure 3.11:** The corona charge deposition rate with 7, 8 and 9 kV applied at the tip of the corona needle.

The distance between the corona needle and the sample has also been varied (see Figure 3.8 for an illustration). The deposition rate decreases with increasing distance and increases when the needle comes in closer proximity of the sample. Although the corona charge deposition rate increases, this goes at the cost of charge uniformity on top of the sample. Therefore the settings used form always a compromise between the corona charge uniformity on the sample and the corona charge deposition rate. For the experiments carried out in Chapter 4, the optimal configuration in terms of corona charge deposition rate and corona charge uniformity is as follows:

- Corona needle positioned 10.5 cm above the sample,
• 9 kV applied to the corona needle,
• Stainless steel grid positioned 5 cm above the sample,
• 10 V applied to the stainless steel grid.

Figure 3.12 shows the corona charge deposition rates for several plasma-assisted ALD Al₂O₃ samples, used in the experiments of Chapter 4 with a thickness of 30 nm for the Al₂O₃ layer. Because the samples are identical, the origin of the difference in corona charge deposition rate has to be found elsewhere. A possible explanation is that depending on the air humidity the corona charge generation rate at the tip of the needle can vary. The dashed lines in Figure 3.12 show the outer limits for the corona charge deposition speed for these samples as obtained during this work. Because the corona charge deposition rate can vary, it is important to keep track of the amount of deposited charge during the measurements at all time.

![Figure 3.12](image-url)

**Figure 3.12:** Corona charge deposition rates for several 30 nm plasma assisted ALD Al₂O₃ samples.

Corona charging experiments for investigating the fixed charge density in thin films typically require 15 – 20 corona charging cycles (illustrated in Figure 3.1) and a full scan takes about 90 – 120 minutes.
3.3 Experimental procedure

3.3.1 Procedure of operation

With all settings in the optimal configuration, corona charging can be used for the investigation of the fixed charge density in thin films. As already mentioned and illustrated in Figure 3.1, the corona charging process uses three experimental setups in a repetitive order. Before depositing the first corona charges on the sample, a first series of surface potential measurements is carried out as a reference. Typically surface potentials in the range of 0.4 – 0.5 V are obtained for a 30 nm thick plasma assisted Al$_2$O$_3$ film before depositing any corona charges. The surface potential is measured at nine positions on the sample, as schematically illustrated in Figure 3.13. These values are then averaged in order to obtain a more reliable value. The measured potential does not only depend on deposited corona charges, but also on the work function difference between the probe and the sample, and the oxide charge density as indicated by equations (2.14) – (2.17). The sample is then transferred to the Sinton lifetime tester and the initial lifetime is determined. This value also serves as a reference, as the field-effect passivation is still unaffected by corona charges. Equation (2.1) allows the obtained lifetime value to be converted to a SRV value.

![Figure 3.13: The nine positions, indicated by the black dots, used for the surface potential measurements on a full 4 inch n-type wafer.](image)

After the initial surface potential and lifetime measurements, the corona charging process is initiated, and the first corona charges are deposited on the surface of the sample. At the peak of the SRV curve, the surface potentials measured are around 5 V for a 30 nm thick plasma assisted Al$_2$O$_3$ film. To further illustrate the corona charging procedure, Figure 4.1 in the next chapter shows the result for an annealed plasma assisted ALD Al$_2$O$_3$ film with a thickness of 30 nm. Depending on the corona charge deposition rate and the amount of data points required for the final plot, intervals of 3-6 minutes of corona charging can be chosen. After a charging interval, the sample is transferred to the Trek 325 electrostatic voltmeter, in order to perform surface another round of potential measurements.
measurements at the same nine points as earlier illustrated in Figure 3.13. The increase in uniformity of deposited corona charges, discussed in Section 3.2.1, allows these surface potential measurements to be performed at the same nine positions as before corona charging. With the average value of the surface potential measurements, the deposited corona charge density can be calculated with equation (2.5). The Sinton lifetime tester is then used for a lifetime measurement again, in order to measure the effect of the deposited corona charge on the lifetime. With one measurement sequence from the three setups, enough data is generated to add one data point to the plot. The corona charging sequence can be repeated in order to obtain the amount of data points necessary to determine the fixed charge density. In Section 4.1.1 is explained how the fixed charge density in the thin Al₂O₃ film can be extracted from the plot.

3.3.2 Sample usage and handling

The corona charge deposited on a sample is not permanent due to the very short atmospheric mean free path (approximately 0.1 µm) of the corona charges \cite{19} and can be removed by a demineralized water rinse. The obsolete water can be blown off with a nitrogen gun, or due to the fragility of the samples, by drying them in an oven at 100 °C. After the rinsing procedure, the initial lifetime can be recovered most of the time, as corona charging is generally considered to be a non-destructive method \cite{20}. Due to the number of transfers between the experimental setups during corona charging experiments, the samples have to be handled with care, as scratches at the edges of the sample can lead to wafer breakage due to the fragility of the wafers.
4. Results & discussion

4.1 Surface passivation properties of thin films

4.1.1 Surface passivation of c-Si by Al₂O₃

A thin Al₂O₃ film with a thickness of 30 nm has been synthesized on a 4 inch n-type c-Si wafer by plasma assisted ALD. By means of corona charging the negative fixed charge density in the Al₂O₃ film was investigated. Figure 4.1 shows the result.

![The corona charging graph from which the fixed charge density in the 30 nm plasma assisted ALD Al₂O₃ film (sample ID: 325) can be extracted. The fixed charge density obtained equals 4.8 \times 10^{12} \text{ cm}^{-2}.

The sample starts with a SRV of ~2 cm/s, which indicates that the sample is very well passivated. Due to the negative fixed charge density in the Al₂O₃ film, electrons are repelled from the c-Si interface. The polarity of the corona charger is set to deposit positive corona charges, creating a positive corona charge density on top of the Al₂O₃ film. The SRV starts to increase, because these positive corona charges begin to compensate the field-effect passivation induced by the negative fixed charge density in the Al₂O₃ film, allowing electrons in the bulk to reach the interface more easily. The SRV will keep on increasing until the positive corona charges reach the same density as the negative fixed charge density in Al₂O₃. At this point the fixed charge density is compensated and the SRV reaches its maximum value, as indicated in Figure 4.1. With
the field-effect passivation nullified, the remaining passivation is of chemical nature. When the positive corona charge density is increased even further by depositing more positive corona charges on top of the sample, the SRV will decrease again, because field-effect passivation is now induced by a net positive charge density, causing holes to be repelled from the c-Si interface. The shape of the peak is not symmetrical due to the asymmetric capture cross section of holes and electrons [22].

The mechanism behind field-effect passivation during corona charging can be illustrated with energy band diagrams, analogous to the ones described in Section 2.4. In Figure 4.1 and 4.2, three regimes are indicated by (a), (b) and (c). In the inversion regime, (a), the positive corona charge density on top of the Al₂O₃ is lower than the negative fixed charge density in the Al₂O₃ film and field-effect passivation is induced by repelling electrons from the interface of the c-Si bulk. In the flatband regime, (b), the positive corona charge density is equal to the negative fixed charge density, nullifying the field-effect passivation and allowing charge carriers to recombine at defect states at the interface. In the accumulation regime, (c), field-effect passivation is induced by a net positive charge density, and now holes are being repelled. When the positive corona charge density becomes sufficiently high, electrons can even become trapped in the Al₂O₃. The trapping of electrons in Al₂O₃ is addressed in more detail in Section 4.2.1.

![Figure 4.2: Field-effect passivation mechanism during the corona charging process: (a) in the inversion regime; (b) in the flatband regime; (c) in the accumulation regime (the black arrow indicates the trapping of electrons).](image-url)
It is now interesting to compare the negative fixed charge density obtained for the plasma assisted Al$_2$O$_3$ film to Al$_2$O$_3$ films deposited by the other deposition techniques, thermal ALD and PECVD (For an overview of the specifications of all the samples used during this work, see Appendix B). Both techniques are used to obtain Al$_2$O$_3$ films with the same thickness of 30 nm. Figure 4.3 compares the negative fixed charge density of Al$_2$O$_3$ films for both deposition techniques to the negative fixed charge density of the plasma assisted ALD Al$_2$O$_3$ sample. For corona charging graphs in this work the dots represent the measured data and the lines are a guide to the eye, unless specified otherwise.

![Figure 4.3: A comparison of the positive corona charge density required to compensate the negative fixed charge density in Al$_2$O$_3$ films with a thickness of 30 nm, synthesized by thermal ALD (sample ID: 389), plasma assisted ALD (sample ID: 325) and PECVD (Sample ID: 316).](image)

Figure 4.3 indicates that thermal ALD Al$_2$O$_3$ contains the lowest negative fixed charge density. Field-effect passivation is already completely nullified when a positive corona charge density of $3.2 \times 10^{12}$ cm$^{-2}$ is reached. For plasma assisted ALD Al$_2$O$_3$ and PECVD Al$_2$O$_3$, positive corona charge densities of $4.8 \times 10^{12}$ cm$^{-2}$ and $6.3 \times 10^{12}$ cm$^{-2}$ are obtained respectively. When the field-effect passivation is nullified, the remaining passivation is of chemical nature. At that point the thermal ALD Al$_2$O$_3$ has a SRV of ~20 cm/s and has therefore the best chemical passivation. The chemical passivation properties of plasma assisted ALD Al$_2$O$_3$ and PECVD Al$_2$O$_3$ are comparable with a SRV of ~125 cm/s.

The graph in Figure 4.3 indicates that thermal ALD Al$_2$O$_3$ has better chemical passivation than plasma assisted ALD Al$_2$O$_3$. The amount of defects at the interface, or the interface defect density $D_{it}$, is comparable for thermal ALD Al$_2$O$_3$ and for plasma...
assisted ALD Al₂O₃ as shown by C-V measurements performed by Dingemans *et al.*[23]. The reason for this difference can be possibly explained when the energy levels of the defect states are taken into account. It has been shown by calculations performed in the PMP group, that corona charging results are consistent with a deeper level of defect states for Al₂O₃ synthesized by plasma assisted ALD as for thermal ALD. Deeper levels (close to midgap) are more efficient carrier trapping centers, leading to higher recombination.

### 4.1.2 Surface passivation of c-Si by SiNₓ as compared to Al₂O₃

The field-effect passivation of c-Si by Al₂O₃ films originates from the negative fixed charge density in the Al₂O₃. Thin films of SiNₓ have, as opposed to Al₂O₃, a positive fixed charge density. To investigate this positive fixed charge density in the SiNₓ film, the polarity of the corona charger is now set to produce negative corona charges. The positive fixed charge density of SiNₓ is then compensated by a negative corona charge density on top of the film. The field-effect passivation of SiNₓ is nullified in the same way as described in section 4.1.1 for Al₂O₃. Figure 4.4 shows a comparison between plasma assisted ALD Al₂O₃ and PECVD SiNₓ.

![Figure 4.4: A comparison between the surface passivation of c-Si by PECVD SiNₓ (sample ID: 7339-3) and plasma assisted ALD Al₂O₃ (sample ID: 325) as obtained by corona charging.](image)

From Figure 4.4 it can be seen that the surface passivation of SiNₓ is being outperformed by the surface passivation properties of plasma assisted ALD Al₂O₃. Before corona charging, the SRV of the plasma assisted Al₂O₃ sample is 2 cm/s, which is lower than the
25 cm/s of the SiN\textsubscript{x} sample. When field-effect passivation is nullified, the plasma assisted ALD Al\textsubscript{2}O\textsubscript{3} sample shows also better chemical passivation, as SRV values of 125 cm/s and 275 cm/s are obtained for Al\textsubscript{2}O\textsubscript{3} and SiN\textsubscript{x} respectively.

### 4.1.3 Surface passivation properties of plasma assisted ALD Al\textsubscript{2}O\textsubscript{3}

The lifetime of charge carriers in c-Si depends on the surface passivation properties of the passivating film. A higher charge carrier lifetime indicates better surface passivation. The lifetime prior to corona charging experiments is a measure for the passivation quality of the thin film and takes chemical as well as field-effect passivation into account. This initial lifetime has been measured with the Sinton lifetime tester for all plasma assisted Al\textsubscript{2}O\textsubscript{3} samples with a thickness of 30 nm for the Al\textsubscript{2}O\textsubscript{3} layer used in this work. The results of these measurements are shown in Figure 4.5.

![Figure 4.5: A plot of initial lifetime and the lifetime with field-effect passivation nullified versus the corona charge density needed for compensating the negative fixed charge density of all plasma assisted ALD Al\textsubscript{2}O\textsubscript{3} samples used in this work.](image)

After the lifetime measurements, corona charging has been performed on the samples in order to obtain the negative fixed charge density. At the compensation point, with the field-effect passivation being nullified, the lifetime indicates the level of chemical passivation provided by Al\textsubscript{2}O\textsubscript{3}. These results are also plotted in the graph shown in Figure 4.5 and are represented by the red dots. It can be seen that the level of chemical passivation is comparable for all samples. The difference in lifetime is therefore given by
the additional negative fixed charge density, which induces higher levels of field-effect passivation. The inset in the top left of Figure 4.5 has the same data plotted, but in SRV values. The lack of a trend (scattered values) for the data shows as well that the increase in initial lifetime cannot be explained by an improved chemical passivation, but rather by a higher field-effect passivation induced by a higher amount of negative fixed charge.

4.1.4 Surface passivation of c-Si by thin film stacks

In this section will be investigated if a stack of materials also provides field-effect passivation. Corona charging experiments have been performed on a PECVD SiO$_x$ / plasma assisted ALD Al$_2$O$_3$ stack and a PECVD SiO$_x$ / thermal ALD Al$_2$O$_3$ stack. In both cases the thickness of the SiO$_x$ layer and Al$_2$O$_3$ layer is 26 nm and 30 nm respectively. The results are shown in Figure 4.6. The corona charging graph of the plasma assisted ALD Al$_2$O$_3$ sample from Figure 4.1 is added for comparison.

For both stacks no maximum value for the SRV is found, indicating that there is no charge present at the interface. In the plasma assisted Al$_2$O$_3$ sample, the negative fixed charge density increases during the anneal treatment. Possibly this increase is caused by electrons tunneling from the c-Si trough the 1.5 nm interfacial native SiO$_x$ layer into the Al$_2$O$_3$. In the case of stacks, the 26 nm SiO$_x$ layer is much thicker, making it nearly

![Figure 4.6: The results of corona charging experiments performed onto Al$_2$O$_3$ / SiO$_x$ stacks (sample ID: 326 & 329). The graph of plasma assisted ALD Al$_2$O$_3$ (sample ID: 325) is added for comparison.](image-url)
impossible for electrons to tunnel through. During the corona charging procedure the SRV slightly increases. This can be attributed to the creation of defects at the interface by trapped electrons induced by the positive corona charge density on top of the sample [21].

4.1.5 Corona charging on as-deposited thermal ALD Al₂O₃

In order to investigate if corona charges can also induce surface passivation, a thermal ALD Al₂O₃ film has been synthesized on a n-type c-Si wafer. After the deposition process, the sample does not receive an anneal treatment. The Al₂O₃ film is therefore referred to as an as-deposited thermal ALD Al₂O₃ film. Figure 4.7 shows the result as obtained by corona charging.

![Figure 4.7](image)

**Figure 4.7:** The results of corona charging experiments performed onto an as-deposited thermal ALD Al₂O₃ film (sample ID: 466). First passivation is induced by the deposited corona charges. At higher corona charge densities, this leads to the creation of defects.

As can be seen from Figure 4.3, well passivated samples start at a SRV of ~2 cm/s. Due to the lack of an anneal treatment, the thermal ALD Al₂O₃ sample in Figure 4.7 starts at a SRV of 30 cm/s. The first deposited corona charges immediately lead to a decrease in SRV, indicating a higher level of surface passivation. The SRV levels off at 15 cm/s where the highest level of surface passivation is obtained. At a corona charge density of $5.5 \times 10^{12} \text{ cm}^{-2}$ the SRV starts to increase again. This can again be attributed to the creation of defects at the interface by trapped electrons induced by higher positive corona charge densities on top of the sample [21].
4.2 Charge manipulation of Al₂O₃ and SiNₓ films

4.2.1 Trapping and de-trapping of electrons into Al₂O₃ films

In Section 4.1.1, a negative fixed charge density of \(4.8 \times 10^{12} \text{ cm}^{-2}\) has been found for an annealed Al₂O₃ film synthesized by plasma assisted ALD, as also shown by the black curve in Figure 4.8. At the end of the black curve, at a positive corona charge density of \(8.7 \times 10^{12} \text{ cm}^{-2}\), there is a net positive charge density of \(3.9 \times 10^{12} \text{ cm}^{-2}\) causing holes to be repelled from the interface.

![Figure 4.8: The results of corona charging experiments performed onto a plasma assisted ALD Al₂O₃ sample (sample ID: 325). The dots represent the first (black squares), second (red circles) and third (green triangles) corona charging scan with positive, negative and positive corona charge polarity respectively.](image)

The polarity of the corona charger is now switched, in order to produce negative corona charges. By depositing these negative corona charges, the SRV starts to increase again, because now the net positive charge density is being compensated, as indicated by the red curve in Figure 4.8. The red curve shows a maximum value for the SRV at a corona charge density of \(6.4 \times 10^{12} \text{ cm}^{-2}\). A first observation of this curve leads to the conclusion that the corona charge density required to nullify the field-effect passivation is higher than the value of \(4.8 \times 10^{12} \text{ cm}^{-2}\) obtained in the first run. This indicates that electrons from the c-Si bulk are additionally trapped into the Al₂O₃ layer. Field-effect passivation is now induced by the negative fixed charge density already present in the Al₂O₃ film, plus the
additionally trapped electrons. The higher SRV however, indicates the creation of defects during the corona charging process. The increased amount of negative charge in the Al₂O₃ cannot compensate for the creation of defects, as the maximum SRV value is with 175 cm/s higher than the 125 cm/s from the first run. At the end of the red curve, at a corona charge density of 3.7·10¹² cm⁻², the polarity of the corona charger is switched back to produce positive corona charges again. The third run shows that some of the additionally trapped electrons can be de-trapped again, as the third peak shifts towards the first one again. The corona charge density required to nullify field-effect passivation now equals 5.8·10¹² cm⁻². By de-trapping some of the trapped electrons, the chemical passivation improves again, indicated by a lower SRV of 160 cm/s.

The question now remains whether all the trapped charge in the Al₂O₃ film can be de-trapped. To investigate this, the second curve representing the deposition of negative corona charges is extended to higher negative charge densities as shown in Figure 4.9. For this experiment another plasma assisted ALD Al₂O₃ sample is prepared under the same conditions and with the same thickness.

![Figure 4.9: The first (black squares), second (red circles) and third (green triangles) corona charging scan of a plasma assisted ALD Al₂O₃ sample (sample ID: 348). The first and third scan are measured with positive corona charge polarity, while the second scan is measured with negative corona charge polarity.](image)

From Figure 4.9 it can be seen that even when the second run is extended to higher negative corona charge densities of -7.8·10¹² cm⁻², still not all of the trapped electrons can be de-trapped, and the same behavior as the previous sample is observed. So once
electrons are trapped, not all of them can be de-trapped again and as a result, the low SRV obtained before corona charging cannot be recovered.

4.2.2 Reversibility of the trapping and de-trapping process

In order to investigate the reversibility of the trapping and de-trapping process, another plasma assisted ALD sample has been prepared under the same conditions as the ones investigated in Section 4.2.1. The thickness of the Al₂O₃ film is also kept the same at 30 nm. Figure 4.10 shows the results of this experiment.

![Figure 4.10](image)

**Figure 4.10:** The results of corona charging experiments performed onto a plasma assisted ALD Al₂O₃ sample (sample ID: 439). The data points represent the successive scans of positive and negative corona charge polarity.

From Figure 4.10 it can be seen that the trapping and de-trapping process can be considered as reversible and stable on the time scale of the experiment, because the position and height of the curves in terms of corona charge density and maximum SRV coincides for successive scans with the same corona charge polarity. This effect can be seen for both negative and positive charging.

4.2.3 Reproducibility of the trapping and de-trapping process

The reproducibility of the experiments performed in Section 4.2.1 can be investigated, when equally prepared samples are compared with one another. As seen in Section 4.1.3,
samples with comparable lifetimes should have the same negative fixed charge density in the Al₂O₃. Figure 4.11 shows the comparison of the first three samples from Figure 4.5, as they have comparable initial lifetimes of 4.8, 5.1 and 5.5 ms respectively.

![Figure 4.11](image-url)

Figure 4.11: Reproducibility of the electron trapping and de-trapping process as obtained by corona charging: (a) during the first run of positive corona charging; (b) during the second run of negative corona charging; (c) during the third run of positive corona charging. (Sample ID: 315, 325 & 348)

The corona charge density required to nullify field-effect passivation is almost identical for all three samples for all three scans. This result is expected because of the comparable initial lifetimes of the samples. The first positive charging run indicates a corona charge density of \( \sim 5.2 \times 10^{12} \text{ cm}^{-2} \) in order to compensate the negative fixed charges in the Al₂O₃. In the second and third run corona charge densities of \( \sim 6.5 \times 10^{12} \text{ cm}^{-2} \) and \( \sim 6.0 \times 10^{12} \text{ cm}^{-2} \) are found respectively. These values are different than the value obtained in the first run due to additional electrons that become trapped and de-trapped in the Al₂O₃ as described in Section 4.2.1.
4.2.4 Trapping and de-trapping on a p-type c-Si wafer

As discussed in Section 4.2.1, at sufficiently high positive corona charge densities on top of a sample, electrons become trapped in the Al$_2$O$_3$ layer. The electrons are accumulated near the interface, as schematically illustrated in Figure 4.2(c). In case of a p-type c-Si wafer this condition is called inversion, as the p-type wafer becomes n-type close to the interface. In Figure 4.12 the results of the corona charging experiments performed on the plasma assisted ALD Al$_2$O$_3$ on top of a p-type c-Si wafer are shown. The same behavior is observed as shown in Figure 4.8 for a plasma assisted ALD Al$_2$O$_3$ film synthesized on a n-type c-Si wafer.

![Figure 4.12](image)

**Figure 4.12:** The result of successive corona charging scans with positive and negative corona charge polarity performed onto a plasma assisted ALD Al$_2$O$_3$ film (Sample ID: 427) synthesized on a p-type c-Si wafer.

4.2.5 Trapping and de-trapping of holes into SiN$_x$

The field-effect passivation properties of SiN$_x$ originate from a positive fixed charge density in the SiN$_x$ film, repelling holes from the interface. In order to perform corona charging experiments, a PECVD SiNx film has been synthesized onto a n-type c-Si wafer. The thickness of the SiN$_x$ layer is 70 nm. The polarity of the corona charger is set to produce negative corona charges in order to nullify the field-effect passivation properties of the SiN$_x$ film. Figure 4.13 shows the results of the corona charging experiments performed onto the SiN$_x$ sample. The positive fixed charge density obtained in the first run equals $2.4 \times 10^{12}$ cm$^{-2}$. At the end of the first run, the polarity of the corona
charge is switched in order to produce positive corona charges. During this second run of corona charging, a positive charge density of $2.9 \times 10^{12}$ cm$^2$ is obtained, indicating that additional holes have become trapped into the SiN$_x$ film. With the polarity of the corona charger set back to produce positive corona charges again, a positive charge density of $2.7 \times 10^{12}$ cm$^2$ is obtained during the third run of corona charging, indicating that some holes are de-trapped.

Figure 4.13: The results of successive corona charging scans with different corona charge polarities performed onto a PECVD SiN$_x$ sample (sample ID: 7339-3). The first scan (black squares) and third scan (green triangles) are measured with negative corona charge polarity. The second scan (red circles) is measured with positive corona charge polarity.

In contrast to the results obtained for Al$_2$O$_3$, the SiN$_x$ film seems to be less sensitive to defect creation during corona charging, as the maximum value in SRV is comparable for all three peaks. The overall passivation quality of this 70 nm thick SiN$_x$ film is being outperformed by 30 nm plasma assisted Al$_2$O$_3$ films, as the SRV at the start is 20 cm/s as compared to 2 cm/s for the Al$_2$O$_3$ films in Figure 4.8. With field-effect passivation nullified and thus with only chemical passivation properties remaining, the SiN$_x$ sample is also being outperformed by the Al$_2$O$_3$ sample with a SRV of 260 cm/s and 125 cm/s respectively at the corona charging peak for the first run of corona charging.

4.3 Thickness dependence of field-effect passivation

Ultrathin films suffer from dielectric breakdown, making corona charging on these samples rather difficult. In this case an additional layer, a so called capping layer, is
added in order to increase the total thickness of the film to make corona charging possible, allowing for the investigation of thickness dependence of the passivation properties. Three $\text{Al}_2\text{O}_3$ samples have been synthesized by thermal ALD. The thickness of the $\text{Al}_2\text{O}_3$ layer is 5, 10 and 30 nm respectively. All samples received an anneal treatment in order to increase the negative fixed charge density in the $\text{Al}_2\text{O}_3$ and to activate their field-effect passivation properties. After the anneal treatment, an additional as-deposited $\text{Al}_2\text{O}_3$ layer is synthesized on top of the films as a capping layer, making the total thickness of the $\text{Al}_2\text{O}_3$ films 50 nm for all samples. The capping layer is deposited at lower temperature ($200 \, ^\circ\text{C}$) as compared to the annealing temperatures ($400 \, ^\circ\text{C}$) of the initial layers, so that the annealed layers are not affected. Figure 4.14 shows the corona charging results.

![Figure 4.14: The results of corona charging experiments performed onto three thermal ALD $\text{Al}_2\text{O}_3$ films with a thickness of 5 nm (black squares), 10 nm (red circles) and 30 nm (green triangles), sample ID: 433, 434 & 435 respectively. While the 10 nm and 30 nm samples show comparable chemical passivation properties, chemical passivation goes down for the 5 nm sample.](image)

As can be seen from Figure 4.14, corona charging is now possible on all three samples, as a maximum in SRV is observed. There is no thickness dependence of the negative fixed charge density, because comparable negative fixed charge densities are obtained for the samples, indicating the same level of field-effect passivation. The chemical passivation properties go down for the 5 nm sample, indicated by a higher peak value for the SRV. Both the 10 nm and 30 nm sample show better chemical passivation properties, which is in agreement with the results of the thermal ALD $\text{Al}_2\text{O}_3$ sample from Figure 4.3.
4.4 Corona charging & second-harmonic generation

4.4.1 Introduction to second-harmonic generation

Second-harmonic generation (SHG) is a nonlinear optical phenomenon that occurs when high intensity radiation interacts with a medium. As a result, light at twice the frequency of the incident radiation is generated \(^2\hbar\omega\), as schematically illustrated in Figure 4.15. Microscopically, SHG can be seen as the conversion of two photons with energy \(\hbar\omega\) into a single photon with energy \(2\hbar\omega\). In first approximation, SHG is forbidden in the bulk of isotropic media, such as c-Si and amorphous materials, due to symmetry considerations. When symmetry is broken, e.g. due to structural changes or the presence of internal electric fields, SHG becomes allowed. Therefore, SHG is highly surface and interface specific, and sensitive to electric fields through the effect of electric-field-induced SHG (EFISH) \(^2\text{[23,24]}\). In case of Al\(_2\)O\(_3\) on Si(100), the SHG intensity can be separated into three components, each contributing to the total intensity. It is possible to distinguish between these contributions, because the silicon band gap slightly changes due to its dependence on the local bonding arrangement. The first contribution originates from the Si-Si interface bonds and the second contribution originates from distorted Si bonds due to the presence of the interfacial SiO\(_x\). There are no contributions to the SHG intensity from the SiO\(_x\) – Al\(_2\)O\(_3\) interface or Al\(_2\)O\(_3\) surface, because the band gaps of SiO\(_x\) and Al\(_2\)O\(_3\) lay outside the available energy range. The third contribution to the SHG intensity is from EFISH, which originates from the space-charge region in the c-Si, as induced by the negative fixed charge in the Al\(_2\)O\(_3\). The amplitude of the EFISH contribution indirectly provides a qualitative measure of the fixed charge density in the film, and thus about the related field-effect passivation properties.

Figure 4.15: Schematic illustration of SHG.

4.4.2 Corona charging & SHG: combining both diagnostics

As discussed in Section 4.4.1, SHG is sensitive to internal electric fields, due to the EFISH contribution to the SGH intensity. When corona charging is performed on the same samples, the EFISH intensity can be related to the fixed charge density, resulting in the quantification of the EFISH intensity in terms of fixed charge density, allowing the fixed charge density to be extracted from the EFISH intensity directly. This is important
for samples on which performing corona charging is difficult, for example samples with a low dielectric strength, such as conductive or ultrathin films. In Figure 4.16, SHG measurements are combined with earlier performed capacitance-voltage (C-V) measurements performed by Dingemans et al. \cite{25}, indicated by the green squares. The EFISH intensity can be obtained by modeling the SHG spectra and the C-V measurements are used to obtain the corresponding fixed charge density of the samples. The black line has been obtained by Terlinden et al. \cite{26} from an analytical model which relates the EFISH intensity to a given charge density. The fixed charge density of the plasma assisted ALD Al\textsubscript{2}O\textsubscript{3}, thermal ALD Al\textsubscript{2}O\textsubscript{3} and PECVD SiN\textsubscript{x} films as obtained with corona charging experiments (see Section 4.1) has also been combined with SHG measurements. The Al\textsubscript{2}O\textsubscript{3} and SiN\textsubscript{x} samples are indicated by the black circles and the red spot respectively. The results are in good agreement with the analytical trend for charge densities obtained by both corona charging and C-V measurements.

![Figure 4.16: The fixed charged density as obtained by corona charging (black circles and red dot) is in good agreement with C-V measurements (green squares) and SHG results as calculated from the theoretical model (black line).](image)

One step further in the process, corona charging can be used to deposit a specific amount of charge on top of a sample. In this way the total charge density and therefore the SHG response can be influenced and controlled, because the total charge density is then formed by the fixed charge density in the film and the corona charge density deposited on top of the sample. Prior to corona charging, a SHG spectrum is measured to obtain the EFISH intensity when only the negative fixed charge density in the Al\textsubscript{2}O\textsubscript{3} film is present.
After the initial SHG measurement, corona charges are deposited onto the sample until a positive corona charge density of $4.7 \cdot 10^{12} \text{ cm}^{-2}$ is reached, as can be seen in Figure 4.17. Because this density is still lower than the negative fixed charge density in the $\text{Al}_2\text{O}_3$ film, no maximum for the SRV has been observed yet and therefore the effective negative charge density is still unknown. Then a second SHG measurement is performed on the sample in order to investigate the effect of the partly compensated negative charge density on the EFISH intensity. During these SHG measurements the corona charge slightly decreases as indicated in Figure 4.17. This is presumably caused by the interaction of the laser from the SHG setup with the applied corona charges. After these SHG measurements, a second run of corona charging is performed. During the second run the peak value for the SRV is found and the negative fixed charge density obtained is $7.1 \cdot 10^{12} \text{ cm}^{-2}$. Because this value is now known, the effective negative charge density at the end of the first run of corona charging can be determined and equals $2.4 \cdot 10^{12} \text{ cm}^{-2}$. When a positive corona charge density of $8.8 \cdot 10^{12} \text{ cm}^{-2}$ is reached at the end of the second run, an effective positive charge density of $1.7 \cdot 10^{12} \text{ cm}^{-2}$ remains and the influence on the EFISH intensity is investigated by another SHG measurement.

After removing the deposited corona charges on top of the sample by a water rinse procedure, as described in Section 3.3.2, the sample is used again for the deposition of corona charges. Before depositing corona charges, again an initial SHG spectrum is

![Graph](image.png)

**Figure 4.17:** The first corona charging experiment used for the corona charger & SHG correlation. An effective negative charge density of $2.4 \cdot 10^{12} \text{ cm}^{-2}$ and an effective positive charge density of $1.7 \cdot 10^{12} \text{ cm}^{-2}$ are obtained in the first and third run respectively. (Sample ID: 440)
obtained as a reference. The sample then receives in the first run of corona charging a positive corona charge density equal to the negative fixed charge density in the sample, making the effective charge density close to zero, as illustrated in Figure 4.18. A second SHG measurement is then performed and it is expected that the EFISH intensity is very low, because of the absence of an effective charge density. After the measurements, a second run of corona charging is performed in order to determine the fixed charge density and to identify the decrease of corona charge density on the sample during the SHG measurement. The second run of corona charging allows the fixed charge density in the Al₂O₃ to be determined at \(7.2 \times 10^{12}\) cm\(^{-2}\).

![Figure 4.18: The second corona charging experiment used for the corona charger & SHG correlation. An effective charge density close to zero is obtained. (Sample ID: 440)](image)

The results from the SHG measurements on the corona charged sample are shown in Figure 4.19. The SHG intensity peaks at 3.4 eV which corresponds to the resonance energy of the bulk c-Si for the E\(_0\)/E\(_1\) interband transition. The EFISH contribution to the total SHG intensity is dominant at higher charge densities\(^{[26]}\) and the EFISH intensity can therefore be approximated from the total intensity. The SHG intensity of the uncharged sample (thus with only the negative fixed charge density in the Al₂O₃) is normalized. The SHG intensity is therefore 1 at a charge density of \(7.1 \times 10^{12}\) cm\(^{-2}\). An effective negative charge density of \(2.4 \times 10^{12}\) cm\(^{-2}\) and an effective positive charge density of \(1.7 \times 10^{12}\) cm\(^{-2}\), should therefore lead to a significant decrease in the SHG intensity, as these effective charge densities are now in the order of 30 % of the normalized SHG intensity. In Figure 4.19, the SHG intensity drops to \(~88\ %\) of the normalized value, indicating a noticeable decrease.
effect of the corona charges, but not with the magnitude expected. An explanation could be that the laser from the SHG setup interacts with the corona charges on top of the sample. Another indication leading to this conclusion is that at the end of a SHG measurement at highest photon energy, a point at 3.3 eV is repeated for comparison, indicating that the SHG intensity increased to the original uncharged value during the measurement. This means that due to influence of the SHG measurement only the negative fixed charge density of the original sample remains.

**Figure 4.19:** The SHG intensity plot of the Al₂O₃ sample with only the negative fixed charge density and with corona charges deposited. With corona charges a decrease in SHG intensity is noticeable.

After the water rinse procedure, the sample was re-used and SHG measurements have been performed on the clean sample. The obtained SHG intensity curve coincides with the first uncharged curve, indicating no negative effect of the water rinsing procedure. Then corona charging is used for depositing a positive corona charge density equal to the negative fixed charge density, resulting in an effective charge density close to zero. The SHG intensity should therefore decrease dramatically, as the internal electric field is nullified. As can be seen in Figure 4.19, the SHG intensity drops to ~88% of the normalized value, again indicating a possible interaction of the laser from the SHG setup with the deposited corona charges.
5. General conclusions

This thesis is concerned with surface passivation of c-Si by the application of a functional thin film on the silicon. In order to investigate the surface passivation properties of these films, a new setup, a so called corona charger, has been developed. The setup has been characterized and it has been demonstrated that two aspects are particularly important for the corona charging process. The first aspect is the uniformity of deposited corona charges on top of the sample. During this work the surface area of the center spot indicating the charge uniformity has been increased from 4 cm$^2$ to 18 cm$^2$, allowing for more accurate lifetime and surface potential measurements. The second important aspect is the corona charge deposition rate, as corona charging experiments can be quite time consuming. At the tip of the needle from the corona charger the surrounding air ionizes and a variation in humidity or composition of the surrounding air can lead to slightly different corona charge deposition rates. Therefore, the corona charge deposition rate has to be monitored over time during the corona charging experiments. It is also found that both aspects are closely related, as an improvement of the corona charge deposition rate often goes at the expense of corona charge uniformity on the sample and vice versa. The chosen settings are therefore always a trade-off between charging speed and uniformity. The optimized settings obtained during the characterization process are presented in this work.

The constructed corona charging setup proved to be a powerful tool for investigating the surface passivation properties of thin films. It is demonstrated that corona charging allows for differentiation between chemical and field-effect passivation, as the field-effect component can be nullified by depositing corona charges of the opposite polarity. The surface passivation properties of Al$_2$O$_3$, synthesized by plasma assisted ALD, thermal ALD and PECVD have been investigated. For thermal ALD Al$_2$O$_3$ a negative fixed charge density of $3.2 \cdot 10^{12}$ cm$^{-2}$ has been obtained. The plasma assisted ALD Al$_2$O$_3$ films showed on average a negative fixed charge density of $5.6 \cdot 10^{12}$ cm$^{-2}$, while PECVD Al$_2$O$_3$ showed the highest negative fixed charge density, with a value of $6.3 \cdot 10^{12}$ cm$^{-2}$. With the field-effect passivation properties nullified, the thermal ALD Al$_2$O$_3$ sample showed the best chemical passivation properties, with the lowest SRV value of 20 cm/s. The chemical passivation properties of plasma assisted ALD Al$_2$O$_3$ and PECVD Al$_2$O$_3$ were found to be comparable, as a SRV peak value of 125 cm/s has been measured for both samples with their field-effect passivation properties nullified.

In addition to Al$_2$O$_3$, also SiN$_x$ films and stacks of SiO$_x$ and Al$_2$O$_3$ have been investigated by corona charging. The field-effect passivation properties of SiN$_x$ originate from a positive fixed charge density and a positive fixed charge density of $2.9 \cdot 10^{12}$ cm$^{-2}$ has been obtained for this material. It is demonstrated that the surface passivation properties of SiN$_x$ are being outperformed by those of Al$_2$O$_3$ as the initial SRV and the SRV with field-effect passivation nullified are higher for the SiN$_x$ samples. For the SiO$_x$/Al$_2$O$_3$ stacks, no peak value for the SRV was obtained, indicating no presence of a negative fixed charge density in the Al$_2$O$_3$ film. A possible explanation is that due to the much thicker SiO$_x$ layer (26 nm as compared to 1.5 nm unintentionally present for a bare
Al₂O₃ film deposited directly on c-Si) electrons are unable to tunnel from the c-Si bulk into the Al₂O₃ layer.

It is also demonstrated that corona charging allows for slight manipulation of the fixed charge density in thin films. At positive corona charge densities beyond the fixed charge density, electrons can become trapped in the Al₂O₃ layer. In that case field-effect passivation is induced by the negative fixed charge density already present in the Al₂O₃ film, plus the additionally trapped electrons. The increased amount of negative charge in the Al₂O₃ however, cannot compensate for the creation of defects due to the high corona charge densities, indicated by higher SRV values. Some of these trapped electrons can be de-trapped, by applying a negative corona charge density on the sample. The initial negative fixed charge density can not be completely recovered. It is also shown that the trapping and de-trapping process is reproducible, as the same corona charge densities and SRV values are obtained for multiple scans with the same corona charge polarity. The SiNx samples show a similar behavior, except that in this case it concerns trapping and de-trapping of holes.

Ultrathin films suffer from dielectric breakdown, making it impossible to examine these samples by means of corona charging. In this work it is demonstrated that by depositing an additional capping layer on top of these ultrathin films, corona charging becomes possible again. Corona charging has been performed on thermal ALD Al₂O₃ samples with a film thickness down to 5 nm, allowing for the investigation of the thickness dependence of the surface passivation properties of these films. Al₂O₃ films with a thickness of 5, 10 and 30 nm have been investigated and it is shown that a comparable negative fixed charge density is obtained for all three samples. The chemical passivation properties however, go down for the 5 nm sample as a higher maximum value for the SRV is found at the fixed charge compensation point, as compared to the thicker films. The surface passivation properties are not affected by the capping layer, as the results for the 30 nm Al₂O₃ sample with capping layer are in good agreement with the results of a bare 30 nm Al₂O₃ sample.

Finally, the corona charging procedure has been combined with SHG measurements on the same samples, in order to quantify the EFISH intensity in terms of fixed charge density. The results obtained by corona charging for the plasma assisted and thermal ALD Al₂O₃ and PECVD SiNx samples are in good agreement with earlier performed C-V measurements and the analytical trend for charge densities obtained from the SHG model. With the extended experiments, where corona charging is used for modifying the effective charge density of a sample, still some questions remain, as the decrease in EFISH intensity is not of the magnitude expected. Possibly, the laser from the SHG setup interacts very locally with the corona charges deposited on the surface of the sample, as the SHG intensity returns to the original uncharged value during the measurement.
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My stay at the Plasma & Materials Processing (PMP) group has been a very pleasant one and I met a lot of enthusiastic and experienced people in the field. Special thanks go to my direct supervisors Magda and Erwin for their excellent guidance during this project. Also many thanks go to Nick, Gijs and Harald for the useful discussions, and cooperation. I also thank all the technicians for their excellent work and assistance regarding the experimental setups. Herman, Janneke, Joris and Ries, thanks a lot!

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At the start of my master I also met a lot of other fellow students, and some of them became truly good friends. We studied many subjects together in the library, ranging from calculus up to quantum mechanics. I would like to thank Kristel, Patryk, Jan-pieter, Jonathan and Joris for all the support and enjoyable things we did together after school time and I think we are friends for life!

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References


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# Appendix A: Trek model 325 specifications

## Performance

<table>
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<th>Measurement Range</th>
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</tr>
</thead>
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<tr>
<td>Accuracy</td>
<td></td>
</tr>
<tr>
<td>Voltage Monitor Output</td>
<td>Better than ±0.05% of full scale.</td>
</tr>
<tr>
<td>Voltage Display</td>
<td>Better than or equal to ±2 counts, referred to the voltage monitor.</td>
</tr>
<tr>
<td>Speed of Response (10% to 90%)</td>
<td>Less than 3 ms for a 10 V step.</td>
</tr>
<tr>
<td>At Fastest Speed Setting</td>
<td>Less than 3 ms for a 10 V step.</td>
</tr>
<tr>
<td>At Slowest Speed Setting</td>
<td>less than 5 ms for a 10 V step.</td>
</tr>
</tbody>
</table>

### Noise (typical)

Less than 1 mV rms, referenced to measured voltage.

### Stability

Drift with Time
- Less than 50 ppm/hour, noncumulative.

Drift with Temperature
- 1:1 monitor output
  - Less than 50 ppm/°C.
- 10:1 monitor output
  - Less than 100 ppm/°C.

## Features

### Null Voltage Source

A precision calibrated ±10 volt source, using a 10-turn potentiometer and dial, can be used to determine the contact potential associated with measured surfaces in reference to the probe sensor's gold electrode as a reference.

<table>
<thead>
<tr>
<th>Range</th>
<th>±10 volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy</td>
<td>±1%</td>
</tr>
<tr>
<td>Resolution</td>
<td>10 mV.</td>
</tr>
</tbody>
</table>

### Voltage Monitor Output (1:1)

A buffered 0 to ±40 V output provides a replica of the measured voltage.

<table>
<thead>
<tr>
<th>Scale</th>
<th>1:1 of the measured voltage.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output Noise</td>
<td>Less than 1 mV rms (measured using the true rms feature of the Hewlett Packard Model 34401A digital multimeter).</td>
</tr>
<tr>
<td>Output Current</td>
<td>5 mA minimum.</td>
</tr>
<tr>
<td>Output Impedance</td>
<td>100 Ω, nominal.</td>
</tr>
</tbody>
</table>

### Voltage Monitor Output (10:1)

A buffered 0 to ±4 V output providing a replica of the measured voltage.

<table>
<thead>
<tr>
<th>Scale</th>
<th>10:1 of the measured voltage.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output Current</td>
<td>5 mA maximum.</td>
</tr>
<tr>
<td>Output Impedance</td>
<td>0.1 Ω, nominal.</td>
</tr>
</tbody>
</table>

## Features (cont.)

### Drift/Spacing Null Adjustment

This back panel adjustment minimizes the variation in monitored voltage values as the probe tip surface spacing changes.

### Voltage Display

3½ digit LED display.

<table>
<thead>
<tr>
<th>Range</th>
<th>0.01 V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 V Range</td>
<td>0.1 V.</td>
</tr>
<tr>
<td>40 V Range</td>
<td>0.1 V.</td>
</tr>
</tbody>
</table>

### Zero Offset

±2 counts, referred to the voltage monitor.

### Sampling Rate

3 readings per second.

### Response Speed Control

A front panel potentiometer that adjusts the AC response of the Model 325.

## Probe

During operation, the metallic surfaces of the probe are driven to voltage levels equal to the measured surface voltage value. A probe holding fixture, should be of an insulating material with dissipative properties (10^7 to 10^10 ohms/square) to prevent shorting of the probe to ground. Phenolic or other dissipative type material is recommended to avoid any fixture material charge retention.

### Recommended Probe-to-Surface Separation

0.2 mm to 2 mm.

### Model PD1126 Sensor Probe

- **Aperture Orientation**: Side viewing.
- **Aperture Size**: 4.6 mm (0.18”).
- **Probe Body Type**: Round body.
- **Dimensions**: 10 mm Diameter x 56 mm L (0.4” Diameter x 2.2” L).
- **Probe Cable Length**: 2743 mm ±127 mm (9 ft ±5”).

### General

- Dimensions: 108 mm H x 223 mm W x 370 mm D (4.25” H x 8.75” W x 14.5” L).
- Weight: 3.6 kg (8 lb).
- **Voltage Monitor Connector**: BNC coaxial connector.
- **Ground Receptacle**: Banana jack.
- **AC Line Cord Receptacle**: Standard three-prong line cord with integral fuse holder.
- **Line Supply**: 90 to 127 V AC at 48 to 63 Hz (optionally available at 180 to 250 V AC at 48 to 63 Hz).
Appendix B: sample specifications

Table A.1 gives an overview of the samples used during this work, together with the specifications of the deposited films.

<table>
<thead>
<tr>
<th>Sample identification number</th>
<th>Deposition method</th>
<th>Film deposited</th>
<th>Thickness of deposited film</th>
</tr>
</thead>
<tbody>
<tr>
<td>315</td>
<td>PA-ALD</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>316</td>
<td>PECVD</td>
<td>Al_2O_3</td>
<td>35</td>
</tr>
<tr>
<td>317</td>
<td>Thermal ALD</td>
<td>Al_2O_3</td>
<td>23</td>
</tr>
<tr>
<td>320</td>
<td>Thermal ALD</td>
<td>Al_2O_3</td>
<td>51</td>
</tr>
<tr>
<td>325</td>
<td>PA-ALD</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>326</td>
<td>PECVD / Thermal ALD</td>
<td>SiO_x / Al_2O_3</td>
<td>26 / 30</td>
</tr>
<tr>
<td>329</td>
<td>PECVD / PA-ALD</td>
<td>SiO_x / Al_2O_3</td>
<td>26 / 30</td>
</tr>
<tr>
<td>348</td>
<td>PA-ALD</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>389</td>
<td>Thermal ALD</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>398</td>
<td>PA-ALD / Thermal ALD</td>
<td>Al_2O_3 / Al_2O_3</td>
<td>5 / 28</td>
</tr>
<tr>
<td>404</td>
<td>PA-ALD (2x annealed)</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>405</td>
<td>Thermal ALD / Thermal ALD</td>
<td>Al_2O_3 / Al_2O_3</td>
<td>30 / 20</td>
</tr>
<tr>
<td>433</td>
<td>Thermal ALD / Thermal ALD</td>
<td>Al_2O_3 / Al_2O_3</td>
<td>5 / 45</td>
</tr>
<tr>
<td>434</td>
<td>Thermal ALD / Thermal ALD</td>
<td>Al_2O_3 / Al_2O_3</td>
<td>10 / 30</td>
</tr>
<tr>
<td>435</td>
<td>Thermal ALD / Thermal ALD</td>
<td>Al_2O_3 / Al_2O_3</td>
<td>30 / 20</td>
</tr>
<tr>
<td>437</td>
<td>PA-ALD (on p-type wafer)</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>439</td>
<td>PA-ALD</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>440</td>
<td>PA-ALD</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>466</td>
<td>PA-ALD (as-deposited)</td>
<td>Al_2O_3</td>
<td>30</td>
</tr>
<tr>
<td>7339-2</td>
<td>PECVD</td>
<td>SiN_x</td>
<td>70</td>
</tr>
<tr>
<td>7339-3</td>
<td>PECVD</td>
<td>SiN_x</td>
<td>70</td>
</tr>
<tr>
<td>7339-4</td>
<td>PECVD</td>
<td>SiN_x</td>
<td>70</td>
</tr>
</tbody>
</table>

Table A.1: An overview of all the samples used during this work.