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Atomic layer deposition of molybdenum oxide for silicon heterojunction solar cells

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Atomic Layer Deposition of Molybdenum Oxide for Silicon Heterojunction Solar Cells

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Abstract

Having a current record efficiency of 24.7% and a potential efficiency of 28%, silicon heterojunction (SHJ) solar cells are a very promising type of solar cell and are therefore receiving considerable interest from the photovoltaics (PV) community. However, one of the limiting factors of the SHJ cell is the parasitic absorption occurring in the front layers of the cell. Especially the hole-selective p-type a-Si:H and passivating intrinsic a-Si:H layers are responsible for substantial losses in generated current, limiting the efficiency of the cell. Recently, MoO$_x$ (x≈3) has been suggested as a viable candidate material to replace the p-type a-Si:H hole-selective layer, on the basis of its wide band gap (∼3 eV) and high work function (∼6.6 eV). Although thermal evaporation was used for the deposition of the MoO$_x$ in the first studies (Battaglia et al, Applied Physics Letters, 2015), atomic layer deposition (ALD) is considered a more suited technique due to its excellent thickness control and the possibility to deposit uniformly over large areas.

In this work, a novel ALD process is reported for the deposition of MoO$_x$, which is compatible with SHJ technology and shows promising results for the application in SHJ solar cells. The newly developed process uses (N'Bu)$_2$(NMe$_2$)$_2$Mo as precursor and O$_2$ plasma as reactant and yields good material properties for deposition temperatures between 50 °C and 350 °C. Between 50 °C and 250 °C amorphous films were deposited at a growth per cycle (GPC) around 0.80 Å, while at higher deposition temperatures the films were polycrystalline and the GPC increased up to 1.88 Å. Rutherford backscattering measurements showed C and N contamination levels below the detection limit of 3 at.% and 2 at.%, respectively, indicating the high quality of the material.

In addition to an extensive study of the ALD process and the resulting material properties, the potential of the novel process for application in SHJ solar cells was explored by depositing ALD MoO$_x$ layers in test structures and using a combination of optical simulations and lifetime measurements. The test structures showed very promising initial results, achieving an implied open-circuit voltage ($V_{oc}$) of 710 mV for a film stack of a-Si:H(i)/MoO$_x$/In$_2$O$_3$:H, with just 3 nm a-Si:H(i). In addition, optical simulations showed an estimated short-circuit current density ($J_{sc}$) of 41.7 mA/cm$^2$ for a solar cell with 5 nm MoO$_x$ as hole selective layer, in contrast to an estimated 40.7 mA/cm$^2$ for the conventional SHJ solar cell with 10 nm a-Si:H(p). Although two very preliminary tests of the ALD MoO$_x$ films in solar cells yielded poor results, additional experiments are planned in order to verify the expected gain in $J_{sc}$ and improved solar cell performance is expected.
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Chapter 1

Introduction

1.1. Silicon heterojunction solar cells

As a consequence of the global demand for more sustainable and cheaper energy, the cumulative installed photovoltaic (PV) capacity increased from 40 GW to 150 GW in the last five years. Moreover, solar cell efficiencies have increased steadily over the last years, with record efficiencies now above 20% for silicon, perovskite, CdTe (Cadmium Telluride) and CIGS (Copper Indium Gallium Selenide) solar cells, as can be seen in Figure 1.1. However, there is still room for improvement and substantial resources are spent on upgrading conventional solar cell designs, such as crystalline silicon cells, and further developing more novel concepts, such as dye-sensitized, organic and perovskite solar cells.

Although several different types of solar cells are available, the market is dominated by the crystalline silicon solar cells, with a current market share around 90%. Moreover, even though non-silicon based solar cells such as the perovskite and CdTe solar cells show promising results, the market will remain dominated by silicon solar cells for the coming years, since the complete PV industry is based around it. For this reason considerable effort is put into the further improvement of silicon solar cells, both in terms of efficiency and costs.

As can be seen in Figure 1.1 an efficiency of 20% was achieved in 1985 for the monocrystalline Si solar cell by UNSW. A record efficiency of 25% was already reached in 1999 and has not been improved ever since. To understand this it is illustrative to review the technology of a conventional c-Si solar cell. To this end, Figure 1.2(a) shows a schematic of a conventional crystalline silicon solar cell. As can be seen, this diffused homojunction solar cell consists of a c-Si base, with a selective electron contact on the front side and a selective hole contact on the back side, formed by phosphorus and aluminum diffused regions, respectively. Ag contacts on the front sides of the solar cell penetrate through the SiN$_x$ antireflection coating (ARC) to extract electrons from the c-Si. These metal-silicon contacts lead to significant recombination of photogenerated electron-hole pairs before they can be extracted from the c-Si and are currently limiting the efficiency of such a c-Si solar cell. Although recently extensive efforts have been made with the Al-BSF (back surface field), PERC (passivated emitter and rear cell) and PERL (passivated emitter and rear locally diffused) c-Si solar cells, the improvements are only limited, while the increasing complexity of the cells makes manufacturing less attractive.
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Figure 1.1. Achieved record efficiencies for different types of solar cells from 1976 to 2015. The (non-concentrating) single crystalline solar cell is indicated in solid blue squares, while the SHJ cell is shown in solid blue circles. (This plot is courtesy of National Renewable Energy Laboratory, Golden, CO.)

A type of solar cell which is especially promising as an alternative to the conventional c-Si solar cell is the silicon heterojunction (SHJ) solar cell (see Figure 1.2(b)), which reached a record efficiency of 24.7% in 2014.\(^{10,11}\) Moreover, in 2015 an efficiency of 25.6% was achieved with a so-called interdigitated back contact (IBC) on the cell (see Figure 1.2(c)), thereby exceeding the record efficiency of the conventional c-Si solar cell. The development of the SHJ solar cell started in the 1990’s at Sanyo, a Japanese electronics company which is currently owned by Panasonic.\(^{12}\) In 1992 Sanyo published a solar cell design, which they called a Heterojunction with Intrinsic Thin layer (HIT), achieving an efficiency of 18%.\(^{13}\) Note that the term SHJ is a more general expression for solar cell structures that contain a heterojunction, such as the HIT cell. Over the years Sanyo succeeded in achieving higher efficiencies and started the production of HIT cells on a mass scale.\(^{12}\) Recently the patent of Sanyo expired and since then more groups are working on further improving the SHJ solar cell. Although since its development the cell design has seen a considerable efficiency increase from 18% to over 25%, the cell has a potential efficiency of 28% and further improvements are expected, leading to the interest of the PV community.\(^{10}\)
Figure 1.2. Schematics of (a) a diffused homojunction solar cell (b) a silicon heterojunction (SHJ) solar cell and (c) a SHJ cell with an interdigitated back contact (IBC).

As can be seen in Figure 1.2(b), a SHJ solar cell consists of a crystalline Si (c-Si) base, passivated on both sides with intrinsic (i) a-Si:H. These a-Si:H(i) layers are necessary to minimize the surface recombination of electron-hole pairs which are generated in the c-Si bulk upon illumination. On the front side of the cell a p-type a-Si:H layer is used as hole selective layer, while an n-type a-Si:H layer is used on the back-side for the collection of electrons. The different a-Si:H layers are generally deposited by plasma-enhanced chemical vapor deposition (PECVD) using SiH$_4$ gas. The p-type a-Si:H layer is doped by adding trimethylboron (TMB) or diborane (B$_2$H$_6$) to the SiH$_4$ gas, while phosphine (PH$_3$) is used to make the a-Si:H an n-type material. In addition to the a-Si:H layers, a transparent conductive oxide (TCO) is used on the front side to conduct charge carriers to the metal contacts. On the back side a TCO is used as an optical reflector to avoid absorption of evanescent waves in the rear metalization. Although several TCO materials exists (ZnO:Al, ZnO:B, SnO), tin-doped indium oxide (In$_2$O$_3$:Sn or ITO) is usually used, because of its high electron mobility. However, recently better alternatives to the conventional tin-doped In$_2$O$_3$ have been found with ALD H-doped In$_2$O$_3$ (In$_2$O$_3$:H) and sputtered Zn-doped In$_2$O$_3$, which are both more transparent than ITO at equal resistivity, leading to more light absorption in the c-Si.

MoO$_x$ in SHJ solar cells

One of the limiting factors of the SHJ solar cells is the parasitic absorption occurring in the front layers of the cell, which leads to a loss in generated current and therefore efficiency. In addition to absorption in the TCO, the major part of this parasitic absorption is a consequence of the relatively low band gap of a-Si:H of around 1.7 eV, which can lead to a loss in generated photocurrent of up to 5%. In order to minimize the losses on the front side of the SHJ cell researchers are looking for more transparent materials to replace the absorbing p-type a-Si:H. Recently MoO$_x$ was introduced by Battaglia et al. as a viable candidate for the replacement of the absorbing p-type a-Si:H layer. MoO$_x$ is much more transparent than a-Si:H, as can be seen in Figure 1.3, and should therefore lead to an increase in generated current when used as a substitute for a-Si:H(p).
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It should be noted that another method to reduce the optical losses is to place both the electron and hole contacts at the back off the cell as is shown in Figure 1.2(c). This design is called the interdigitated back contact (IBC) and completely reduces the absorption losses due to the p-type a-Si:H layer and shading by the metal contacts on the front of the cell. Several groups have worked on this concept and in 2014 Sanyo/Panasonic reached an efficiency of 25.6% with a IBC-SHJ cell.\textsuperscript{22–26} However, the deposition of the p-type and n-type contacts next to one another requires complex processing, such as masking and etching, making the design less attractive for industry.

![Figure 1.3. Absorption coefficients of a-Si:H and MoO\textsubscript{x}. On the right axis the photon flux for the standard AM1.5g spectrum is shown for reference.](image)

In Figure 1.4 a comparison is made between the losses in short-circuit current ($J_{sc}$) on the front side of a conventional SHJ cell and a cell with MoO\textsubscript{x} as hole selective layer, which were estimated using the optical constants as shown in Figure 1.3 in an optical simulator. More details on optical simulations to calculate the losses on the front side of a solar cell will be given in Section 3.2.3. Three mechanisms contribute to these losses, which are free carrier reflection (FCR) and free carrier absorption (FCA) due to conducting electrons in the TCO and parasitic absorption in the passivation and hole selective layers. As can be seen in Figure 1.4 up to 2.1 mA/cm\textsuperscript{2} of the incoming 44.0 mA/cm\textsuperscript{2} in photocurrent is lost in the intrinsic and p-type a-Si:H layers combined, whereas only 1 mA/cm\textsuperscript{2} is lost when MoO\textsubscript{x} is used as hole selective layer.

Battaglia indeed showed a substantial improvement of 1.9 mA/cm\textsuperscript{2} in $J_{sc}$ when replacing the conventional p-type a-Si:H with a layer of 10 nm thermally evaporated MoO\textsubscript{x}.\textsuperscript{20} However, thermal evaporation is not a well suited technique for the deposition of very thin, conformal layers, as was also stated by Battaglia.\textsuperscript{19} A more suitable technique for the deposition of such layers is atomic layer deposition, as will be explained in the next section.
1.2. Atomic layer deposition

Atomic layer deposition (ALD) is a thin film deposition technique, which is based on sequential, self-limiting surface reactions.\textsuperscript{27, 28} Because of the self-limiting character of the technique, ultimate thickness control on the atomic scale is possible. To deposit a film by ALD, the surface is exposed to a number of cycles, each consisting of two, or in some cases more, half-cycles (see Figure 1.5). During the first half-cycle a vaporized precursor material reacts with groups on the surface of the substrate. After reaction of the precursor with the substrate the newly formed surface groups are unreactive with the precursor molecule, which causes the process to be self-limiting. After purging of the reactor, a different reactant is introduced in the second half-cycle, which reacts with the ligands of the absorbed precursor molecules, again in a self-limiting manner. By repeating this process the film is deposited one submonolayer at a time, until the desired thickness is achieved. The growth rate of an ALD process is generally expressed in the thickness increase per cycle, i.e. growth per cycle (GPC) and by choosing the right amount of cycles the thickness of the layer can be precisely controlled.
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Figure 1.5. Schematic of an ALD cycle for the deposition of $\text{Al}_2\text{O}_3$ using trimethylaluminum (TMA) and $\text{H}_2\text{O}$. Precursor absorption occurs in the first half-cycle, after which the ligands of the precursor are removed in the second half-cycle in the reaction with $\text{H}_2\text{O}$.

A typical setup used for ALD can be seen in Figure 1.6 and consists of a vacuum chamber connected to a turbopump and several gas inlets to enable the insertion of different gases and precursors. To allow for the use of a plasma as reactant in the second half-cycle, the chamber is connected to an inductively coupled plasma (ICP) source. Compared to thermal ALD, where the reactant is introduced in the gaseous form and the required energy is delivered to the substrate in the form of thermal energy, plasma-assisted ALD (PA-ALD) can offer the benefit of an increased growth rate at low temperatures and lower impurity incorporation, due to the additional energy of the plasma species.

Figure 1.6. Schematic overview of the ALDii reactor used for the deposition of MoO$_x$ thin films. An inductively coupled plasma source is placed above the substrate table, which enables exposure of the substrate to several different plasmas. The precursor is contained in a stainless steel bubbler and Ar used is typically used as carrier gas. A spectroscopic ellipsometry (SE) system is mounted on the reactor, allowing for in situ SE measurements.
1.2. Atomic layer deposition

A wide range of both in situ and ex situ diagnostics is available to study ALD processes and atomic-layer-deposited films. An extremely powerful tool is spectroscopic ellipsometry (SE), which is used to monitor the thickness of the films in situ during growth and to characterize the optical properties of the deposited film. SE works by measuring the change in the polarization state of a light beam upon reflection on a sample, which is dependent on the material properties and the film thickness. Other important characterization techniques include X-ray photoelectron spectroscopy (XPS), which is used to study the chemical composition; X-ray diffraction (XRD), which gives information about the crystallinity; and atomic force microscopy (AFM) to analyze the surface morphology. Moreover, Raman spectroscopy can be used to study the microstructure of thin films and scanning— and transmission electron microscopy enable the imaging of the deposited films on nanometer scale, which is especially interesting for 3D structures.

ALD of MoO$_x$

Since its development in the 1970’s ALD has been used for the deposition numerous materials, using a wide range of different precursors and reactants, and extensive overviews can be found in literature. In order to find a suitable process for the deposition of MoO$_x$ in SHJ solar cells, an overview of existing MoO$_x$ ALD processes was made:

- Diskus et al. (2010) reported the first MoO$_x$ ALD process and used molybdenum hexacarbonyl (Mo(CO)$_6$) as precursor and a combination of ozone and water as reactants for the deposition of MoO$_3$. This process yields a GPC of around 0.75 Å, within a very narrow temperature window of 157 °C to 172 °C.

- Tseng et al. (2013) deposited metallic Mo films using MoF$_6$ and Si$_2$H$_6$ at 200 °C. The Mo films were subsequently post-treated with ozone to form MoO$_3$ for application as anode buffer layer in organic photovoltaic cells. Although the cells showed good results, this process is not ideal, since it is a two step process and uses a halide precursor.

- Recently Bertuch et al. (2014) used bis(tert-butylimido)-bis(dimethylamido)molybdenum ((N’Bu)$_2$(NMe)$_2$Mo) and ozone to deposit MoO$_3$, achieving a relatively high GPC of 1.3 Å at a deposition temperature of 300 °C. However, at low deposition temperatures the process yielded a low GPC and substantial amounts of C and N in the films. The chemical structure of the (N’Bu)$_2$(NMe)$_2$Mo is shown in Figure 1.7.
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Because all three reported processes are not ideal for application in SHJ solar cells, due to contamination in the films, too high deposition temperatures, or a relatively low GPC, it was decided to develop a new ALD process. Since the \( (\text{N}^t\text{Bu})_2(\text{NMe}_2)_2\text{Mo} \) precursor showed a promising GPC and good material qualities at high deposition temperatures in the process reported by Bertuch, it was the precursor of choice for this project. However, to enable the deposition of good quality films at low temperatures, which is required for the SHJ cell, \( \text{O}_2 \) plasma instead of \( \text{O}_3 \) was used as reactant. The \( (\text{N}^t\text{Bu})_2(\text{NMe}_2)_2\text{Mo} \) precursor shows a good thermal stability and provides sufficient vapor pressure, making it a good candidate for ALD.\(^{36}\)

Moreover, the precursor has also proven its potential in the deposition of MoN, using ammonia as reactant.\(^{37}\) Disadvantages of the precursor might be its relatively large size and the fact that it contains large amounts of C and H (see Figure 1.7), which might lead to impurity incorporation in the films.

\[\text{ALD for PV}\]

The key merits of ALD, i.e. uniformity, digital thickness control, conformality and relatively low deposition temperatures, make ALD a perfect candidate for the deposition of thin films for application in solar cells.\(^{38,39}\) The use of ALD for photovoltaics started already in 1994 with the deposition of GaAs, AlGaAs and AlAs as absorber layers in multijunction solar cells.\(^{40,41}\)

More recently, in 2006, ALD found its use for the deposition of \( \text{Al}_2\text{O}_3 \) surface passivation layers, which are now getting introduced in manufacturing.\(^{38,42,43}\) Moreover, other metal oxides that are commonly used in solar cells such as \( \text{ZnO}, \text{In}_2\text{O}_3, \text{TiO}_2 \) and \( \text{HfO}_2 \) have been deposited by ALD and are increasingly applied in solar cell devices.\(^{16,44,45}\) As was already mentioned, recently \( \text{In}_2\text{O}_3:H \) has been deposited by ALD using \( \text{InCp} \) as precursor, leading to excellent material properties and is expected to lead to a gain in \( J_{sc} \) of the SHJ solar cell.\(^{46}\)

Although more applications are expected, large scale manufacturing in industry is not possible with the conventional ALD reactors used in research. Fortunately new developments in the ALD field, such as batch ALD and spatial ALD, enable fast deposition of large areas and ALD is therefore expected to find a more widespread application in the PV industry within the next few years.\(^{47-50}\)

\[\text{Figure 1.7. Schematic of the (N}^t\text{Bu})_2(\text{NMe}_2)_2\text{Mo precursor which will be used in combination with O}_2 \text{ plasma for the deposited of MoO}_x \text{ films.}\]
1.3. Project goals

The long term goal of this project is to use high-quality, uniform MoO$_x$ films deposited by ALD as hole selective layers in SHJ solar cells. MoO$_x$ will be used as a replacement for the currently used p-type a-Si:H hole selective layer, which limits the efficiency of the SHJ solar cell due to parasitic absorption. However, in order to make this possible a decent ALD process for the deposition of MoO$_x$ needs to be developed. Therefore the goals of this project can be specified as follows:

- Develop an ALD process for the deposition of MoO$_x$ films, compatible with SHJ technology. The process should yield high-quality films at low deposition temperatures, since the a-Si:H layers in SHJ solar cells require process temperatures below 200 °C.

- Study the dependence of the growth process and the material properties on the deposition temperature in detail. Fully characterize the deposited material in terms of chemical composition, optical properties and crystallinity.

- Assess the potential of the newly developed ALD process for application in SHJ solar cells by the deposition of MoO$_x$ films in application-relevant test structures and a combination of optical simulations and minority carrier lifetime measurements.

1.4. Outline of this thesis

This thesis is divided into two main chapters. In Chapter 2 the ALD process development is discussed, including a detailed characterization of the deposition process and the material properties. This chapter has been submitted for publication in Journal of Vacuum Science & Technology A as 'Atomic layer deposition of molybdenum oxide from (N'Bu)$_2$(NMe)$_2$Mo and O$_2$ plasma' by Vos et al. Additional information that goes beyond the scope of this publication is supplied in a separate section directly after Chapter 2, entitled 'Supplementary Info Chapter 2'. Chapter 3 deals with the application of the newly developed ALD process to SHJ solar cells. Parts of this chapter were published as 'Low temperature atomic layer deposition of MoO$_x$ for silicon heterojunction solar cells' in Physica Status Solidi Rapid Research Letters, Vol. 9, Issue 7 by Macco et al. Chapter 3 is again followed by a section with additional info (Supp. Info. Chapter 3), after which a general conclusion on the project and outlook to further research will be given in Chapter 4.
Abstract: Molybdenum oxide (MoO$_x$) films have been deposited by atomic layer deposition using bis(tert-butylimido)-bis(dimethylamido)molybdenum ((N$^t$Bu)$_2$(NMe$_2$)$_2$Mo) and oxygen plasma, within a temperature range of 50 °C to 350 °C. Amorphous film growth was observed between 50 °C and 200 °C at a growth per cycle (GPC) around 0.80 Å. For deposition temperatures of 250 °C and higher a transition to polycrystalline growth was observed, accompanied by an increase in GPC up to 1.88 Å. For all deposition temperatures the O/Mo ratio was found to be just below 3, indicating the films were slightly substoichiometric with respect to MoO$_3$ and contained oxygen vacancies. The high purity of the films was demonstrated by the absence of detectable C and N contamination in Rutherford backscattering measurements, and a H content varying between 3 at. % and 11 at. % measured with elastic recoil detection. In addition to the chemical composition, the optical properties as determined by spectroscopic ellipsometry are reported as well.

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M.F.J. Vos, B. Macco, N.F.W. Thissen, A.A. Bol and W.M.M. Kessels, submitted for publication
Chapter 2. Process Development

2.1. Introduction

Molybdenum trioxide has received considerable interest due to its optical, electrical and catalytic properties.\textsuperscript{51–54} Thin films of MoO\textsubscript{3} are being used in gas sensors\textsuperscript{55,56}, solid state lithium batteries\textsuperscript{57} and in the synthesis of MoS\textsubscript{2} by sulfurization\textsuperscript{58}. Moreover, recently MoO\textsubscript{3} has been used in organic photovoltaics (OPV)\textsuperscript{35}, perovskite solar cells\textsuperscript{59} and silicon solar cells as hole extraction layer\textsuperscript{19–21}. A wide range of deposition techniques has been employed for the growth of MoO\textsubscript{3} films, such as thermal evaporation,\textsuperscript{60} electron beam evaporation\textsuperscript{61}, sputtering\textsuperscript{62–64}, chemical vapor deposition (CVD)\textsuperscript{65} and atomic layer deposition (ALD)\textsuperscript{34,35}. Of these techniques, ALD offers the advantages of uniform and conformal growth, in conjunction with atomic level thickness control, merits which are highly desirable for some of the abovementioned applications. However, only few reports on ALD of MoO\textsubscript{3} can be found in literature. Diskus et al. deposited MoO\textsubscript{3} by ALD using molybdenum hexacarbonyl, Mo(CO)\textsubscript{6}, as precursor and simultaneous doses of ozone and water as reactants.\textsuperscript{34} However, the thermal stability of the Mo(CO)\textsubscript{6} precursor limited the ALD window to 152 °C - 172 °C. Another study used MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} for the ALD of molybdenum films, which were subsequently post-treated with UV/ozone to obtain fully oxidized MoO\textsubscript{3}.\textsuperscript{35} However, the fact that this is a two-step process that involves the use of a halide precursor, makes this process less ideal. More recently Bertuch et al. reported an ALD process to deposit MoO\textsubscript{x} using bis(tert-butylimido)-bis(dimethylamido)molybdenum, (N\textsubscript{t}Bu)\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2}Mo, as the metal-organic precursor and ozone as reactant.\textsuperscript{36} This process promisingly shows a high growth per cycle (GPC) of ∼1.3 Å at 300 °C, but suffers from a low GPC and from C and N contamination in the films at lower deposition temperatures of 150 °C to 200 °C. Previously the (N\textsubscript{t}Bu)\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2}Mo precursor has also been used by Miikkulainen et al. to grow films of molybdenum nitride using ammonia as reactant.\textsuperscript{37} In this study we report on an ALD process to deposit high-purity substoichiometric molybdenum trioxide (MoO\textsubscript{3-x}) films using the (N\textsubscript{t}Bu)\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2}Mo precursor and O\textsubscript{2} plasma, for a wide temperature range of 50 °C - 350 °C. O\textsubscript{2} plasma can offer the advantage of reasonable growth rates at lower deposition temperatures. In recent work, we have already shown the potential of this process for the deposition of selective hole contacts for silicon heterojunction solar cells.\textsuperscript{56} Here, we focus on a detailed study of the ALD process and material properties, such as chemical composition and optical properties.

2.2. Experimental details

2.2.1. Film deposition

MoO\textsubscript{x} films were deposited in a home-built ALD reactor ("ALDi"), consisting of a vacuum chamber connected to an inductively coupled plasma (ICP) source and a pump unit. The pump unit consists of a rotary and turbomolecular pump reaching a base pressure of ∼10\textsuperscript{-6} Torr. An extensive description of the reactor can be found in earlier work from our group.\textsuperscript{29} The typical processing conditions and experimental settings are summarized in Table 2.1. The set temperature of the substrate table was varied between 50°C and 350 °C. The temperature of the reactor wall was maintained at 100 °C, for all depositions, except for depositions at a table temperature...
of 50 °C, for which the wall temperature was set to 50 °C. The liquid \((\text{NtBu})_2(\text{NMe}_2)_2\text{Mo}\) precursor (98%, Strem Chemicals) was contained in a bubbler at 50 °C, at which it is reported to have a vapor pressure of 0.13 Torr.\(^{36}\) The chemical structure of the precursor can be seen in the inset of Figure 2.1. The precursor supply line was heated to 80 °C to prevent condensation of the precursor and Ar was used as a carrier gas. All depositions were done on Si (100) wafers with native oxide.

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The standard ALD recipe consists of precursor dosing for 6 s in the first half of the ALD cycle. Ar gas is used as a carrier gas during the precursor dose, resulting in a chamber pressure of 7.5 mTorr. Subsequently the reactor is purged with Ar for 3 s and pumped down for 3 s. The second half-cycle consists of \(\text{O}_2\) plasma exposure with a plasma power of 100 W at a chamber pressure 5.1 mTorr for 4 s.

2.2.2. Film analysis

The growth of the MoO\(_x\) films was monitored \textit{in situ} by spectroscopic ellipsometry (SE) using a J.A. Woollam, Inc. M2000U ellipsometer. The dielectric function of the deposited films was parameterized using a combination of a Tauc-Lorentz and a Gaussian oscillator, as will be addressed later in this paper. X-ray photoelectron spectroscopy (XPS) was done with a Thermo Scientific KA1066 spectrometer, using monochromatic Al K\(\alpha\) X-rays with an energy of 1486.6 eV. Rutherford backscattering spectroscopy (RBS) and Elastic recoil detection (ERD) were performed by AccTec BV, Eindhoven, The Netherlands, using a Singletron with a 2 MeV He\(^+\) beam to determine the chemical composition of the films. The mass density was calculated using the areal mass density as obtained from RBS/ERD measurements and the film thickness as obtained from SE. Raman spectroscopy measurements were done using a Renishaw Invia Raman Microscope, using a laser wavelength of 514 nm. Gracing incidence X-ray diffraction (XRD) measurements were done with a PANalytical X’Pert Pro MRD system, using Cu K\(\alpha\) X-rays (\(\lambda = 1.54 \text{ Å}\)). Scanning electron microscopy (SEM) images were obtained using a FEI Nova600i NanoLab.
2.3. Results and discussion

2.3.1. ALD growth

To study the ALD process as a function of the deposition temperature, a set of approximately 20 nm thick samples was deposited at temperatures between 50 °C and 350 °C, using a standard saturated precursor dosing time of 6 s and a plasma exposure time of 4 s. In Figure 2.1 the film thickness is shown as a function of ALD cycles for temperatures between 50 °C and 350 °C. The thickness of the deposited films proceeds linearly with the number of ALD cycles for deposition temperatures of 50 °C and 200 °C, corresponding to a GPC of ~0.8 Å. For temperatures of 300 °C and 350 °C a gradual increase in GPC during film growth can be observed, which is attributed to a transition from amorphous to polycrystalline growth. Such a transition has been observed before for other ALD processes before, for instance for the deposition of TiO$_2$.\textsuperscript{67,68} A transition from amorphous to polycrystalline growth is accompanied by the appearance of grains, very likely leading to an increase in surface area and therefore to an increase in GPC.\textsuperscript{69} This will be further corroborated in Section 2.3.2, where the crystallinity and morphology of the films will be discussed. Note that in addition to the increased roughness, an enhanced reactivity of the polycrystalline surface can also contribute to the increase in GPC. To exclude the presence of a thermal CVD component as a possible explanation for the enhanced growth rate at higher deposition temperatures, it was verified that no growth occurs when using O$_2$ gas instead of O$_2$ plasma as reactant.

![Figure 2.1. Thickness of the MoO$_x$ film, measured with in situ SE, as a function of ALD cycles for deposition temperatures between 50 °C and 350 °C. A precursor dosing time of 6 s and plasma exposure time of 4 s were used. A transition from amorphous to crystalline growth can be observed for 300 °C and 350 °C by a gradual increase in GPC during film growth. The inset shows the chemical structure of the (N$\text{tBu}$)$_2$(NM$_2$)$_2$Mo precursor used for the deposition.](image-url)
2.3. Results and discussion

In Figure 2.2 the saturation curves for the precursor dose step (Figure 2.2(a)) and plasma exposure time (Figure 2.2(b)) are shown for various temperatures. The GPC as a function of precursor dosing time (Figure 2.2(a)) shows a relatively soft saturation and a precursor dosing time of 6 s was chosen as standard. The plasma saturation curve (Figure 2.2(b)) shows a slightly higher GPC for low plasma exposure times, likely corresponding to incomplete combustion of precursor ligands or redeposition. To assure complete combustion of ligands and to prevent impurity incorporation in the films a plasma exposure time of 4 s was chosen as standard.

![Figure 2.2](image_url)

**Figure 2.2.** (a) Precursor saturation curve showing the growth per cycle (GPC) as a function of precursor dosing time for a constant plasma exposure time of 4 s. For both 50 °C and 200 °C saturation occurs after approximately 6 s. (b) Plasma exposure saturation curve for a deposition temperature of 100 °C depicting the GPC as a function of plasma exposure time. The precursor dosing time was kept constant at 6 s. The lines serve as guides to the eye.

In Figure 2.3 the GPC as a function of deposition temperature is shown, both in terms of thickness, determined from SE, and in terms of deposited Mo atoms/nm², determined from RBS. Note that the samples used for determination of the GPC data in Figure 2.3 correspond to the samples used in Figure 2.1 and had a thickness of ~20 nm. As can be seen in Figure 2.3 the GPC determined by SE (closed squares) varies only slightly for temperatures between 50 °C and 200 °C. At these deposition temperatures the films are completely amorphous, as will also be shown in Section 2.3.2. For higher temperatures the GPC increases, which is due to a transition to polycrystalline growth. For a deposition temperature of 300 °C a distinction can be made between amorphous growth at the start of the deposition, and polycrystalline growth at a larger film thickness. The GPC determined from the first 20 to 100 cycles was found to be 0.93 Å, while calculating the GPC from the last 50 cycles of the deposition at 300 °C yields a GPC of 1.25 Å. Note that these values for the GPC were calculated by determining the slope at different positions on the curves in Figure 2.1. Since at 350 °C the amorphous-polycrystalline transition occurs already at a very early stage, only the GPC for polycrystalline growth is reported for this temperature. Figure 2.3 also shows the GPC in terms of the number of deposited Mo atoms/nm² (open circles), as determined from RBS, which shows an increase with temperature. Note that this value was determined ex situ by dividing the total number of Mo atoms/nm² by the number of ALD cycles. The value is therefore an average over all the
ALD cycles used to deposit the film. For this reason this quantity is denoted as \(<\text{GPC}_{\text{RBS}}\>\). For a direct comparison of the RBS and SE data, also the average GPC as determined from SE (\(<\text{GPC}_{\text{SE}}\>\), which is the final film thickness divided by the total number of cycles, is shown in Figure 2.3 (open squares). As can be seen, there is a very strong correlation between \(<\text{GPC}_{\text{RBS}}\>\) and \(<\text{GPC}_{\text{SE}}\>\), which demonstrates that the increased GPC at high temperatures is mainly caused by an actual increase in the number of deposited Mo atoms per cycle and not by a decrease in film density. This increase in GPC at high temperatures is thought to be caused by an increase in surface area due to increased roughness, an increased reactivity of the surface, or a combination of both.\(^{69}\)

Figure 2.3. GPC in terms of thickness from \textit{in situ} SE (left axis) and GPC in terms of deposited Mo atoms/nm\(^2\) (right axis) from ex situ RBS, as a function of deposition temperature. The open circles show the average GPC in terms of deposited Mo atoms/nm\(^2\), determined by division of the total Mo atoms/nm\(^2\) by the number of ALD cycles. The open squares depict the average GPC (\(<\text{GPC}_{\text{SE}}\>\), determined from the final thickness and the number of cycles, while the solid squares show the final GPC (GPC\(_{\text{SE}}\)), determined using the \textit{in situ} data of the last 50 cycles of the deposition. A distinction can be made between amorphous and polycrystalline film growth. For a deposition temperature of 300 °C, both a GPC for amorphous growth, determined before the onset of polycrystalline growth (<100 cycles), and a GPC for crystalline growth, determined from the last 50 cycles, are displayed. The lines are a guide to the eye. The relative error in the measured number of Mo atoms is 2%.

\(\text{2.3.2. Film characterization}\)

In this section, the chemical composition, morphology and optical properties of the ~20 nm films deposited at temperatures between 50 °C and 350 °C will be discussed. The most important film properties have been summarized in Table 2.2.
2.3. Results and discussion

Chemical composition

From RBS/ERD measurements both the stoichiometry and the elemental composition were determined. The O/Mo ratio and the atomic percentage of H as a function of deposition temperature can be found in Table II. The O/Mo ratio was found to be below 3 for all investigated deposition temperatures (2.9 on average), indicating the films were slightly substoichiometric with respect to molybdenum trioxide (O/Mo ratio = 3). Note that the samples were transferred in ambient and therefore an effect of ambient on the film stoichiometry cannot be excluded. For all deposition temperatures the contents of C and N impurities were below the detection limit of 3 at. % and 2 at. %, respectively, showing the high quality of the films. No substantial C or N contamination is present in the bulk of the films, which is in line with the fact that there is no indication of thermal decomposition of the precursor molecule for high decomposition temperatures. The H content of the films deposited at 50 °C and 100 °C was found to be around 10 at. %, which decreased to ~5 at. % for higher temperatures. This H can originate from the ligands of the precursor molecule, which contains 30 H atoms, as well as from residual water in the reactor.

Table 2.2. Properties of MoO$_x$ films for deposition temperatures 50 °C – 350 °C, as determined from RBS, SE and XPS. The thickness of the films was approximately 20 nm. The number of deposited Mo at. nm$^{-2}$ cycle$^{-1}$ and chemical composition were determined from RBS, the refractive index and the Tauc band gap ($E_g$) from SE and the density from combining the RBS and SE results. C and N contamination in the bulk were below the RBS detection limit of 3 at. % and 2 at. % respectively. Typical errors are indicated in the top row and in the third row for the H content.

<table>
<thead>
<tr>
<th>Deposition temperature (°C)</th>
<th>GPC (Å)</th>
<th>Mo (at. nm$^{-2}$ cycle$^{-1}$)</th>
<th>O/Mo</th>
<th>[H] (at. %)</th>
<th>Mass density (g cm$^{-3}$)</th>
<th>Refractive index (at 1.96 eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.83 ± 0.03</td>
<td>1.41 ± 0.05</td>
<td>2.9 ± 0.1</td>
<td>11 ± 1</td>
<td>3.9 ± 0.2</td>
<td>2.11 ± 0.03</td>
<td>2.87 ± 0.03</td>
</tr>
<tr>
<td>100</td>
<td>0.72</td>
<td>1.42</td>
<td>2.8</td>
<td>10</td>
<td>4.3</td>
<td>2.20</td>
<td>2.80</td>
</tr>
<tr>
<td>150</td>
<td>0.74</td>
<td>1.37</td>
<td>2.9</td>
<td>3.3 ± 0.4</td>
<td>4.2</td>
<td>2.19</td>
<td>2.81</td>
</tr>
<tr>
<td>200</td>
<td>0.80</td>
<td>1.47</td>
<td>2.9</td>
<td>3.3</td>
<td>4.2</td>
<td>2.18</td>
<td>2.80</td>
</tr>
<tr>
<td>250</td>
<td>0.93</td>
<td>1.52</td>
<td>3.0</td>
<td>3.6</td>
<td>4.2</td>
<td>2.13</td>
<td>2.77</td>
</tr>
<tr>
<td>300</td>
<td>1.25</td>
<td>1.84</td>
<td>2.9</td>
<td>4.3</td>
<td>4.2</td>
<td>2.12</td>
<td>2.92</td>
</tr>
<tr>
<td>350</td>
<td>1.88</td>
<td>2.48</td>
<td>2.9</td>
<td>4.1</td>
<td>3.9</td>
<td>1.98</td>
<td>2.92</td>
</tr>
</tbody>
</table>

The mass density of the films was calculated using the RBS/ERD measurements and the layer thicknesses from SE. For deposition temperatures from 100 °C to 300 °C the density was found to be around 4.2 g cm$^{-3}$, which is somewhat lower than the bulk density of crystalline MoO$_3$ of 4.69 g cm$^{-3}$. The density is slightly lower (3.9 g cm$^{-3}$) for 50 °C and 350 °C. X-ray photoelectron spectroscopy (XPS) was used to further study the chemical composition of the deposited films. In Figure 2.4(a) the Mo3d peak is depicted for a deposition temperature of 50 °C and 350 °C. It was found that sputtering of MoO$_x$ with Ar$^+$ ions causes a change in stoichiometry of the
material due to preferential O sputtering (see Section 2.C), which is known from literature.\textsuperscript{71} For this reason the XPS data in Figure 2.4 was collected prior to any sputtering and thus the presence of surface contamination cannot be excluded.

![Figure 2.4](image_url)

**Figure 2.4.** XPS core level spectra for Mo3d (a) and O1s (b) for MoO\textsubscript{x} deposited at 50 °C and 350 °C. The data was obtained prior to Ar sputtering to avoid reduction of Mo to lower oxidation states.

The Mo3d XPS spectrum in Figure 2.4(a) shows a dominant doublet with the Mo3d\textsubscript{5/2} peak at \(\sim 233.0\) eV and the Mo3d\textsubscript{3/2} peak at 236.2 eV, corresponding to the fully oxidized Mo\textsuperscript{6+} state, i.e. MoO\textsubscript{3}.\textsuperscript{71,72} The binding energy of the Mo3d\textsubscript{5/2} peak is slightly higher than other literature reports of 232.2 eV - 232.8 eV, which is likely an effect of surface charging.\textsuperscript{63,71} A second doublet at 231.7 eV and 235.0 eV is required to obtain a good fit to the experimental data. This doublet has previously been attributed to the M\textsuperscript{5+} state, corresponding to oxygen vacancies.\textsuperscript{19,73} For instance, Battaglia \textit{et al.} demonstrated an increase in the Mo\textsuperscript{5+} peak upon annealing the samples in N\textsubscript{2} environment, whereas no change was observed when annealing in O\textsubscript{2} environment.\textsuperscript{19} Similar experiments were carried out in this study and yielded similar results (see Supplementary Info 2.C). The presence of oxygen vacancies is also consistent with the substoichiometric O/Mo ratio as was found with RBS. The O1s peak in Figure 2.4(b) consists of a dominant peak at approximately 530.9 eV, corresponding to O bound to Mo atoms\textsuperscript{71} and a small shoulder around 532.5 eV, which could possibly be explained by O-H bonds\textsuperscript{73} or by absorbed surface species.\textsuperscript{63} Although the presence of C and N was observed in the XPS spectrum, their signals were almost completely absent after shortly sputtering with Ar\textsuperscript{+} ions. This indicates that C and N were mainly present on the surface, which is consistent with the RBS results.

**Crystallinity and surface morphology**

Raman spectroscopy and XRD were used to assess the crystallinity of the films as a function of the deposition temperature. From Figure 2.5(a) it can be seen that the film deposited at 250 °C shows two peaks, at 777 cm\textsuperscript{-1} and 849 cm\textsuperscript{-1}, corresponding to the metastable monoclinic \(\beta\)-crystal phase.\textsuperscript{74,75} For 300 °C and 350 °C a clear peak is visible at 818 cm\textsuperscript{-1}, indicating the
2.3. Results and discussion

Films are in the stable orthorhombic α-phase. The absence of these peaks for temperatures of 200 °C and lower confirms their amorphous nature. The XRD spectra in Figure 2.5(b) show similar results of crystalline films at higher deposition temperatures. The (110) peak in Figure 2.5(b) corresponds to the β-phase, while the (020), (040) and (060) peaks originate from the α-phase. For 200 °C and 250 °C no peaks are visible, corresponding to amorphous material. Although Raman spectroscopy shows crystallinity for a deposition temperature of 250 °C it is thought that the bulk material is amorphous and some small crystallites are present at the surface of the film. This can also be seen in the SEM images in Figure 2.6.

![Figure 2.5.](image)

**Figure 2.5.** (a) Raman spectra of the MoO$_x$ films deposited at temperatures between 50 °C and 350 °C, for films of approximately 20 nm thick. At 250 °C the monoclinic β-phase of MoO$_3$ is visible, while films deposited at 300 °C and 350 °C show features of the orthorhombic α-phase. (b) XRD spectra of the MoO$_x$ films deposited at temperatures between 200 °C and 350 °C. For 300 and 350 °C distinct peaks are visible, corresponding to crystalline material, while the spectra for lower temperatures indicate the films are amorphous. The spectra are offset vertically for clarity.

The film morphology as a function of deposition temperature was studied by top-view SEM (Figure 2.6). For a deposition temperature of 50 °C a relatively smooth surface is observed, corresponding to amorphous film growth. At 250 °C some small nuclei are visible, surrounded by amorphous material. The film deposited at 300 °C contains many, larger crystallites, but amorphous material is still visible in the background. For 350 °C the surface of the film appears fully crystalline. The appearance of crystallites and increasing crystallinity at higher temperatures is in agreement with the Raman data as presented in Figure 2.5, as well as the observations made based on Figure 2.1. Moreover, the increased roughness at higher deposition temperatures was also confirmed with atomic force microscopy (see Section 2.A), which showed a RMS roughness of 0.2 nm for 50 °C versus 1.9 nm for 350 °C.
Chapter 2. Process Development

Optical properties

The optical properties of the MoO\(_x\) films have been analyzed using SE. A Tauc-Lorentz oscillator was used to account for interband absorption. Additionally, a Gaussian oscillator at low photon energy (\(\sim\)1 eV) was used for absorption inside the band gap, likely caused by defects. This absorption at low photon energy has been reported earlier for MoO\(_x\) and has been attributed to oxygen defects.\(^{19, 54, 62, 77}\) The refractive index \((n)\) and the extinction coefficient \((k)\) obtained from the modeling are shown in Figure 2.7.

The refractive index in Figure 2.7 lies in the 1.8 - 2.2 range, which is consistent with other literature on MoO\(_x\).\(^{62, 78}\) Although the extinction coefficient \(k\) varies only slightly with deposition temperature, the refractive index \(n\) is strongly dependent on the deposition temperature, likely caused by differences in density. From the absorption coefficient \(\alpha\) obtained from the SE measurements the Tauc band gap was determined by plotting \((\alpha hv)^{1/2}\) as a function of photon energy (considering MoO\(_x\) is an indirect band gap material) and extrapolating the linear part to zero absorption (see Section 2.B).\(^{79}\) The results of this procedure are listed in Table II. The obtained band gap values of 2.7 eV - 2.9 eV are in the range of the values of 2.5 eV - 3.0 eV previously reported in the literature.\(^{51, 52, 78, 80}\) For deposition temperatures of 300 °C and 350 °C a slightly higher band gap of 2.9 eV than for lower deposition temperatures was found, which is in line with the polycrystalline nature of the material.
2.4. Conclusion

An ALD process to deposit high-purity MoO$_x$ films has been presented, which is based on (N$^t$Bu)$_2$(NMe$_2$)$_2$Mo dosing and O$_2$ plasma exposure and which yields a high growth per cycle (GPC) over a temperature range of 50 °C to 350 °C. For amorphous growth at low temperature (<250 °C) GPC values of 0.72 Å to 0.93 Å were obtained. For higher deposition temperatures a transition to polycrystalline growth occurs, which is accompanied by an increase in GPC up to 1.88 Å for 350 °C. It was shown that this increase in GPC is consistent with an increase in the amount of deposited Mo at. nm$^{-2}$ cycle$^{-1}$. For all deposition temperatures the MoO$_x$ films were found to be slightly substoichiometric with respect to MoO$_3$. Contamination by C and N was determined to be below the RBS detection limit of 3 at. % and 2 at. % respectively, which shows the high quality of the material. In addition, the MoO$_x$ films contain 3 at. % - 11 at. % hydrogen. The Tauc band gap was found to vary between 2.77 eV and 2.87 eV for amorphous films and was 2.92 eV for polycrystalline films deposited at 300 °C and 350 °C. Due to the high purity of the films and the relatively high GPC, the presented process is likely suitable for many applications, such as photovoltaics and other optoelectronic devices.
Supplementary Info Chapter 2

2.A. Atomic force microscopy

The transition from amorphous to polycrystalline growth that was described in Section 2.3.2 is accompanied by the appearance of grains, which very likely leads to an increased surface roughness. This increase in roughness is thought to be accompanied by an increase in surface area, which causes an increased growth rate. Although the top-view SEM images in Figure 2.6 indeed seem to indicate an increased roughness, they only show a 2D projection of the surface. For this reason atomic force microscopy (AFM), which gives information about the 3D structure of the film, was used to quantitatively study the surface morphology. The AFM images in Figure 2.8 show a very smooth surface for a deposition temperature of 50 °C, with a root-mean-square roughness of 0.2 nm, while a roughness of 1.9 nm is found for 350 °C. Since Raman measurements showed that films deposited at temperatures above 250 °C are crystalline, the AFM images indeed confirm the hypothesis that the appearance of grains leads to a higher surface roughness.

![AFM images](image)

**Figure 2.8.** Atomic force microscopy (AFM) images of MoO$_3$ samples deposited at 50 °C and 350°C for a scan area of $2 \times 2$ µm$^2$. The root-mean-square roughness is 0.2 nm for the sample deposited at 50 °C and 1.9 nm for a deposition temperature 350 °C. The thickness of the films was approximately 20 nm. Note that the vertical scales are different.

In addition to the SEM and AFM images, cross-sectional TEM could be used to get a better understanding of the crystal growth. As was discussed in Section 2.3.1 a transition was observed from amorphous to polycrystalline growth during film growth at high deposition temperatures, meaning the deposited material starts out as amorphous, while crystalline material is deposited as the thickness of the films increased. A cross-sectional TEM image would yield information
about the vertical grain size, and would therefore tell if the amorphous bottom part of the film is crystallized as well in the amorphous to polycrystalline transition (a so-called solid phase crystallization process), or if it remains amorphous.

2.B. Band gap determination

A standard procedure to determine the optical band gap of a material is to use the absorption coefficient $\alpha$ obtained from the SE data and plot $(\alpha \nu)^n$ as a function of photon energy. Here, $n = 1/2$ is used for an indirect band gap material (such as MoO$_3$), while $n = 2$ corresponds to a direct band gap. By extrapolating the linear part to zero absorption the Tauc band gap can then be extracted from this so-called Tauc-plot. The Tauc-plots which were used for the determination of the band gap can be seen in Figure 2.9. The calculated band gap of 2.7 eV - 2.9 eV is in agreement with reported literature values of 2.7 - 3.2 eV. For deposition temperatures of 300 °C and 350 °C a slightly higher band gap of around 2.9 eV was found, in line with the polycrystalline nature of the material.

![Figure 2.9. Tauc plots depicting $(\alpha \nu)^{1/2}$ as a function of photon energy for deposition temperatures of 50 °C, 200 °C and 350 °C. (inset) Band gap of the MoO$_x$ films as a function of deposition temperature.](image)

2.C. X-ray photoemission spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique which uses the photoelectric effect to determine the elemental composition of a material. This is done by irradiating a surface with an X-ray source and simultaneously collecting the core electrons that are ejected from the atoms in the top $\sim$10 nm of the surface. By measuring the kinetic energy $E_k$ of the ejected electrons, the binding energy $E_B$ can be calculated according to $E_k = h\nu - E_B - \Phi$, where $h\nu$ is the energy of the X-rays (1486.6 eV for Al-K$\alpha$ radiation) and $\Phi$ is the work function of the spectrometer. This $E_B$ gives information about the chemical composition and can be used to identify the elements in the material, since the different electron states within an atom give rise
to a binding energy spectrum which is typical of that atom. Moreover, from the exact position of the spectrum peaks the chemical state of the atom can be determined.

Normally a sample is sputter-cleaned with Ar\(^+\) ions to remove surface contamination prior to XPS measurements. However, as was stated in Section 2.3.2 MoO\(_x\) is reduced upon sputtering, which can lead to incorrect analysis of the measurements. This can be seen in Figure 2.10(a), which shows the Mo3d peak for different etch levels, which correspond to longer Ar\(^+\) ion exposure time. As can be seen the as deposited material was MoO\(_3\) before any Ar\(^+\) sputtering and is reduced to MoO\(_2\) and even metallic Mo.\(^{71}\) The fact that the first level shows a clear MoO\(_3\) peak and not a mixture of multiple oxidation states indicates that the difference in the measured Mo3d peak is not due to a change in stoichiometry but is a consequence of the sputtering. Note that the peak for etch level 0 is distorted due to the fact that there was a layer of In\(_2\)O\(_3\):H on top of the MoO\(_x\).

In Section 2.3.2 it was discussed that the shoulder at 231.7 eV in the Mo3d XPS spectrum corresponds to the Mo\(^{5+}\) state and was indicative of oxygen vacancies in the material. To confirm this the sample was annealed in N\(_2\) environment for 30 s at different temperatures, upon which the shoulder increased in intensity, as can be seen in Figure 2.10(b). In addition to the Mo\(^{5+}\) state, the Mo\(^{4+}\) state becomes visible after the anneal at 400 °C, which increases further upon the anneal at 500 °C.\(^{19,71}\)

![Figure 2.10](image1.png)

Figure 2.10. (a) XPS after sputtering with Ar\(^+\) ions for different etch levels. One etch level corresponds to an Ar\(^+\) time of 30 s. (b) XPS Mo3d peak after annealing in N\(_2\) for 30 seconds at 300 °C, 400 °C and 500 °C.\(^{19,71}\)

### 2.D. XPS work function determination

As was explained in Section 2.C, XPS measures the kinetic energy of electrons escaping a surface that is being irradiated with X-rays. Considering that the energy of the incoming photons is well defined (1486.6 ± 0.2 eV), the measured kinetic energy can be used to calculate the work function of a material, which is the energy required to travel from the Fermi level to the vacuum
level. Since the work function of a material is of importance in many applications such as solar cells and other optoelectronic devices where it influences the band alignment, knowing and controlling the work function of a material can be very useful. In this Section first the principle of this method will be explained, followed by a discussion on measurements of the work function of MoO\textsubscript{x} and its challenges.

To understand the principle of work function measurements by XPS it is important to be aware of the difference between primary and secondary photoemission electrons. Primary electrons have not suffered from inelastic collisions before they left the sample and result in distinct spectral features, which are used for the normal elemental XPS analysis and characterization of the valence band. Secondary electrons, on the other hand, have lost energy due to inelastic scattering in the sample and have a continuous energy spectrum. A schematic of an XPS spectrum with both the primary and secondary electrons is shown in Figure 2.11(a).

![Figure 2.11.](image)

Figure 2.11. (a) XPS spectrum showing the valence band, core level and secondary electrons, shown in blue. A second spectrum, shown in pink, originates from secondary electrons generated in the analyzer and is superimposed on the spectrum from the sample. (b) & (c) XPS spectra where a bias is applied to the sample to separate the analyzer electrons from the sample electrons, for a Au reference sample and a semiconductor respectively. Due to an electrical contact the Fermi level of the sample is equilibrated to the Fermi level of the metal sample. By defining the internal energy scale according to $E_k = h\nu - E_B$, it follows that the Fermi level $E_F$ corresponds to zero binding energy, while electrons at the secondary electron cut-off have a binding energy of $E_B = h\nu - \Phi$, where $h\nu$ is the X-ray photon energy and $\Phi$ is the work function of the sample. Note that for the semiconductor there are no electronic states between the valence band maximum (VBM) and $E_F$. (This figure has been adapted from Schlaf.\textsuperscript{81})
As can be seen in Figure 2.11(a), the secondary electron spectrum shows an abrupt cut-off in the high energy region, which corresponds to the electrons that had just enough energy to overcome the work function of the material. Since their kinetic energy was equal to the work function before they left the sample, the position of this cut-off can be used to determine the work function of a material. However, a second spectrum overlaps with the spectrum of the electrons from the sample, which originates from secondary electrons generated in the XPS analyzer, as is shown in Figure 2.11(a). To separate the two spectra and to determine the cut-off value of the sample spectrum, a negative bias is applied to the samples. This bias accelerates the electrons leaving the sample towards the analyzer, resulting in a higher kinetic energy, while the electrons generated in the analyzer are not affected by the bias (see Figure 2.11(b) and (c)).

After the two different spectra have been separated by the bias, the measured kinetic energy can be used to determine the work function. As said in Section 2.C the relation between the measured kinetic energy and the binding energy of the electrons is given by \( E_k = h\nu - E_B - \Phi_A \). However, the work function of the analyzer \( \Phi_A \) is not exactly known. For normal XPS measurements this is solved by calibrating the complete spectrum to the C1s peak at a binding energy 284.8 eV. For work function measurements, however, this is dealt with by using a Au reference sample of which the Fermi level is calibrated to zero binding energy, as is also done in Figure 2.11(b). It makes sense to do this, since the fastest electrons are primary electrons which originate directly from the Fermi level, corresponding to zero binding energy. Before these electrons leave the surface, they have a kinetic energy which is equal to the incoming photon energy \( h\nu \). This definition thus corresponds to the internal kinetic energy of the electrons, i.e. before they left the sample, given by \( E_k = h\nu - E_B \). From this definition it follows that electrons at the secondary electron cut-off had a binding energy of \( E_B = h\nu - \Phi \), since prior to leaving the sample their kinetic energy was \( \Phi \). So by determining the binding energy of the cut-off, the work function can be calculated.

Due to an electrical contact between the sample and the sample holder, the Fermi level of the measured sample is equilibrated to the Fermi level of the Au reference sample, as is shown in Figure 2.11(c). This is required since the position of the Fermi level cannot be determined individually in a semiconductor with this method. So by doing this the position of the secondary electron cut-off can be used to calculate the work function \( \Phi \) according to \( E_B = h\nu - \Phi \). Note that using inverse photoelectron spectroscopy (IPES) the ionization energy and electron affinity of a material can be determined in a similar way, since this technique enables the analysis of the conduction band instead of the valence band. \(^{82}\)

Figure 2.12 shows the procedure which is followed for the work function determination. First the exact position of the Fermi level of the Au sample is found by determining the inflection point near the onset of the valence band, i.e. the position were the first derivative of the intensity is maximum and the second derivative is zero. Secondly, the Fermi level of the Au sample is shifted to zero binding energy, while simultaneously the other spectra are shifted by the same value. The work function is then found by extrapolating the linear region of the cutoff to zero intensity and subtracting this energy from the X-ray photon energy. As can be seen in Figure 2.12 a work function of around 5.1 eV is found for the Au reference sample, which corresponds
In order to automate the work function calculation a Matlab script was written, which can be found in Appendix A. This script reads in the data of the Au reference sample and the sample of interest and then finds the correction value needed to shift the spectra. It subsequently performs a linear fit at the secondary electron cut-off, in order to find the correct value for the cut-off and uses this value to calculate the work function. Finally the shifted spectra and the calculated work function values are plotted and the data is saved to an Excel file for further processing.

![Diagram](image)

**Figure 2.12.** Secondary electron cut-off (a) and valence band spectrum showing the density of states at the Fermi level (b) for a Au reference sample. The work function is determined as follows: 1. The position of the Fermi level is determined, which corresponds to the inflection point near the valence band edge. 2. The spectra are shifted by a value of 29.7 V in order to calibrate the Fermi level of the Au sample to zero binding energy. 3. A linear fit is performed at the secondary cut-off to determine the cut-off value. 4. The difference between the secondary electron cut-off and the photon energy gives the work function: a work function of approximately 5.1 eV is found, which corresponds to literature. The sample was shortly cleaned with Ar$^+$ ions to remove surface contamination.

To check the XPS work function measurement procedure, several metals were investigated. In Figure 2.13(a) the secondary electron cut-off spectra for high-purity Cu foil (used as substrate for graphene deposition), ALD Pd, ALD Pt and the standard Au reference sample can be seen. In addition, Figure 2.13(b) shows the valence band spectra of the different metals, of which the Fermi levels are equilibrated at zero binding energy. The cut-off values found from Figure 2.13(a) were used to calculate $\Phi_M$ as shown in Table 2.3. As can be seen in Table 2.3, the measured work functions for these metals correspond well to reported literature values. Note that the uncertainty in the X-ray photon energy is 0.2 eV.
2.D. XPS work function determination

Table 2.3. Measured work functions $\Phi_M$ and literature values $\Phi_L$ for several metals (left) (Au, Pt, Pd and Cu) and metal oxides (right) (MoO$_x$, In$_2$O$_3$:H and TiO$_2$). All samples were deposited by ALD, except for the standard Au reference sample and the Cu sample, which was a piece of high-purity Cu foil. Note that the standard error in $\Phi_M$ is 0.2 eV.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Phi_M$ (eV)</th>
<th>$\Phi_L$ (eV)</th>
<th>Material</th>
<th>$\Phi_M$ (eV)</th>
<th>$\Phi_L$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>5.1</td>
<td>5.1</td>
<td>MoO$_x$ (As-deposited)</td>
<td>4.3 - 4.8</td>
<td>5.5</td>
</tr>
<tr>
<td>Pt</td>
<td>5.1</td>
<td>5.1 - 6.0</td>
<td>MoO$_x$ (UV-O$_3$ treated)</td>
<td>5.2</td>
<td>6.6</td>
</tr>
<tr>
<td>Pd</td>
<td>5.0</td>
<td>5.1</td>
<td>In$_2$O$_3$:H</td>
<td>4.0</td>
<td>4.5 - 5.0</td>
</tr>
<tr>
<td>Cu</td>
<td>4.5</td>
<td>4.7</td>
<td>TiO$_2$</td>
<td>3.9</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Figure 2.13. (a) & (b) Secondary electron cut-off (a) and density of states at the Fermi level (b) for high-purity Cu foil, ALD Pd, ALD Pt and the standard Au reference sample. (c) & (d) Secondary electron cut-off (c) and density of states at the Fermi level (d) for MoO$_x$ deposited at 50 °C and 350 °C and for a Au reference sample. The measurements on as-deposited films are shown in solid lines, while the dashed lines are after Ar sputtering. For the MoO$_x$ samples a magnification (10x) of a range of the spectra around the Fermi level is shown for clarity. A small defect-derived band is visible inside the band gap for the as-deposited samples, which is dramatically increased upon Ar sputtering. The spectra are offset vertically for clarity.

Work function of ALD MoO$_x$

After $\Phi_M$ was successfully measured for several metals, $\Phi_M$ of the ALD MoO$_x$ was measured using the same procedure. Figure 2.13(c) and (d) show the secondary electron cut-off for MoO$_x$ samples deposited at 50 °C and 350 °C. For MoO$_x$ a $\Phi_M$ of approximately 4.5 eV was found prior to Ar sputtering for all deposition temperatures, which is substantially lower than reported literature values of around 5.5 eV for surface contaminated MoO$_3$. Although Vasilopoulou et al. showed that both oxygen vacancies and hydrogenation can cause the work function of MoO$_x$ to decrease, a difference of 1 eV is thought to be too large.$^{73}$ From the literature it is well known...
that the work function of MoO$_x$ is highly sensitive to surface contamination, and can lead to a reduction in work function to $\sim$5.5 eV as compared to $\sim$6.6 eV for clean MoO$_x$.\textsuperscript{19,82,89} However, since Ar sputtering of MoO$_x$ causes the reduction to lower oxidation states, sputtering should not be used for the cleaning of the surface. An alternative to clean the surface prior to the measurements is an UV-O$_3$ treatment, as will be discussed later. Nevertheless, the spectra that were obtained after Ar cleaning are added for reference, showing a large increase in defect states within the band gap (see Figure 2.13(d)). Note that for the as-deposited samples a very small defect-derived band is visible inside the band gap as well, corresponding to the oxygen vacancies which were observed with XPS and SE. Vasilopoulou \textit{et al.} observed similar defect states for oxygen-deficient and hydrogenated MoO$_x$ and correlated them to the work function, showing that they can be used to tune the band alignment in a heterostructure.\textsuperscript{73}

In order to check the work function measurement on MoO$_x$ a thermally evaporated MoO$_x$ sample was used as a reference (data now shown).\textsuperscript{*} This measurement resulted in an extremely low value of 3.9 eV, whereas normally evaporated MoO$_x$ has a work function around 5.5 eV, for a contaminated surface.\textsuperscript{19,82} This is an indication that it is not the ALD MoO$_x$ that has a low work function, but rather the measurement method which results in an incorrect value. To check this hypothesis $\Phi_M$ was measured for several other metal oxides deposited by ALD. As can be seen in Table 2.3, incorrect values for $\Phi_M$ were also found for In$_2$O$_3$:H and TiO$_2$.

After thorough investigation of the literature on work function measurement by the use of XPS it was found that several people report on similar issues. Yi \textit{et al.} showed that a low intensity X-ray source is needed for the correct measurement of the work function of ITO (In$_2$O$_3$:Sn) and that for normal intensity the measured work function decreases with exposure time.\textsuperscript{90} Moreover Gutmann \textit{et al.} reported the same effects for work function measurements of TiO$_2$ using UPS (UV photoemission spectroscopy). In addition they claimed that the UV exposure induces adsorption of OH-groups, which leads to formation of a surface dipole, causing a reduction of the workfunction.\textsuperscript{91} Battaglia \textit{et al.} successfully measured a work function of 6.6 eV for clean MoO$_x$ using XPS and stated that the measurements were obtained using low X-ray intensity and an enlarged distance between sample and analyzer.\textsuperscript{19} Although there are several reports on these issues, it is not exactly clear what the exact mechanism is that causes the work function reduction. Kugler \textit{et al.} suggested it is "an effect of changes in the oxygen defect distribution", while Yi \textit{et al.} claim it is "likely caused by the formation of a surface dipole due to a photochemical reaction of the sample with surface contamination".\textsuperscript{90,92} Another likely possible explanation is the build-up of positive charge due to incomplete replenishment of the emitted electrons.\textsuperscript{91} It is however clear that measuring the work function using XPS or UPS is not a straightforward task and careful consideration is needed to obtain a correct value.

Considering the reports on the effect of the X-ray exposure time and intensity of the X-ray source, several additional test measurements were performed. Firstly, the number of scans over which is averaged to obtain a smooth signal was decreased from 10 to 1 scan. This results in an increase of the noise level in the measured spectra, but still gives an acceptable signature of the cut-off edge. Secondly, the dwell time was decreased from 50 ms to values between 10 ms and 1 ms and the work function was measured for several dwell times. This was done at different

\textsuperscript{*}Martijn Tijssen from Delft University of Technology is gratefully acknowledged for providing the reference sample.
locations on the sample to avoid effects of previous measurements. Note that the dwell time is the time that is taken to measure one point in the electron energy spectrum, and decreasing the dwell time also leads to an increase of the noise. Unfortunately the Thermo Scientific KA1066 XPS setup which is used for the measurements does not enable lowering the X-ray intensity or variation of the height between the sample and the X-ray source.

Figure 2.14. (a) Secondary electron cut-off for an as-deposited sample and a sample after 1.5 h UV-O$_3$ treatment, using just 1 scan and a dwell time of 5 ms. (b) Secondary electron cut-off for different dwell times between 10 and 1 ms.

Figure 2.14(a) shows the electron cut-off for MoO$_x$ measured using just 1 scan and a dwell time of 5 ms. This resulted in a measured value of 4.8 eV, which is just slightly higher than the 4.5 eV which was measured with the standard measurement settings (10 scans and 50 ms dwell time). In addition to the as-deposited sample, a sample which had been treated with UV-O$_3$ for 1.5 h is shown in Figure 2.14(a). Such a UV-O$_3$ treatment is often done prior to XPS measurements to remove adventitious contamination from the surface of the sample, since it leads to the decomposition of organic species.$^{93,94}$ Battaglia and Meyer reported an increase in the work function of MoO$_x$ from 5.5 eV to 6.7 eV upon UV-O$_3$ treatment.$^{20,82}$ However, for the measurements shown in Figure 2.14 the treatment only resulted in an increase of the measured work function of $\sim$ 0.4 eV. This might be caused by the short ($\sim$ 5 min) air exposure of the sample after the UV-O$_3$ treatment before loading the sample into the XPS setup. Battaglia mentioned that the reported 6.6 eV was measured after an in vacuo UV-O$_3$ treatment inside the XPS setup and that very short air exposure would already lead to a decrease in work function.$^{95}$

In Figure 2.14(b) the electron cut-off is plotted for different dwell times, using just 1 scan for the acquisition. As can be seen, the measured work function increases with decreasing dwell time, indicating the X-ray exposure is indeed affecting the work function of the sample. Since the work function still increases when going from 3 ms to 1 ms, it is assumed the exposure time is still too long or, equivalently, the intensity of the X-ray source is too high. Based on Figure 2.14 it can be concluded that the X-ray intensity is too high. Unfortunately varying the X-ray intensity is not possible in the Thermo Scientific KA1066 setup and another XPS setup or another method, such as a Kelvin probe, should be used for the correct measurement of the work function. However, after optimizing the measurement procedure a work function of 4.8
eV was found for In$_2$O$_3$:H, which does correspond to the expected literature value and indicates the effect of the X-ray exposure is material dependent.$^8$1

**2.E. Process development on OpAL™ reactor**

After the MoO$_x$ ALD process was successfully developed on the home-built ('ALDii') reactor, it was decided to also develop the process on an OpAL™ reactor from Oxford instruments, which will also be used for Al$_2$O$_3$ and In$_2$O$_3$:H depositions as discussed in Chapter 3. This will be more convenient for the solar cell fabrication, since it enables the deposition of the In$_2$O$_3$:H TCO directly on top of the MoO$_x$, without the need to break the vacuum and expose the MoO$_x$ films to ambient. This is of importance since it is well known that the work function of MoO$_x$ is highly sensitive to adventitious carbon and water absorption upon air exposure. Moreover, the use of the OpAL reactor for the MoO$_x$ deposition is beneficial since the OpAL reactor is located in a clean room, while the ALDii is not and will enable the use of larger wafers (8” versus 4”).

![Figure 2.15. Saturation curves for the precursor dosing time (a) and plasma exposure time (b) for MoO$_x$ depositions on the OpAL™ reactor. The saturation curves obtained on the home-built reactor are added for reference. Note that the precursor saturation curve for the home-built reactor corresponds to a deposition of 150 °C, since it was not available for 100 °C.](image)

Figure 2.15 shows the precursor and plasma saturation curves for both the OpAL reactor and the home-built ALDii reactor for deposition temperatures of 100 °C and 150 °C. As can be seen, similar saturating behavior was found, and it was decided to keep a precursor dosing time of 6 s and a plasma exposure time of 4 s. However, on the home-built reactor a GPC of 0.72 Å was found, while on the OpAL™ reactor the GPC is 1.21 Å. For an ideal ALD process, this difference is not expected, since the number of adsorbed precursor molecules should be the same after saturation has been reached, independent of the reactor. However, differences in GPC have been reported before for the same ALD processes done on different reactors. As will be discussed below, large amounts of impurities (C, N & H) are present in the films, which are thought to be the cause of the high GPC. Moreover, an interesting observation is that
Bertuch et al. reported a GPC up to 1.3 Å using the same precursor in combination with ozone, which is in line with the GPC of 1.2 Å found on the OpAL reactor. Note that an important difference between the two reactors is that the home-built is equipped with a turbopump, while the OpAL reactor is not. As a result of this, the chamber pressure during the ALD process is \( \sim 135 \text{ mTorr} \) on the OpAL, whereas in the home-built reactor it is only 7.5 mTorr. Possibly the higher pressure in the OpAL reactor leads to a different reaction mechanism or the higher level of background water in the OpAL enhances the growth. Note that the existence of a CVD component was excluded by exposing the surface to \( \text{O}_2 \) gas instead of \( \text{O}_2 \) plasma during the second half-cycle of the process, which yielded no film growth.

To study the elemental composition of the MoO\(_x\) films XPS measurements were performed. As can be seen in Figure 2.16(a), XPS showed similar results to the results from the ALDii reactor and the Mo3d peak confirmed that the material is again slightly substoichiometric with respect to MoO\(_3\). This was also found in RBS measurements, of which the results can be seen in Table 2.2. Figure 2.16(b) shows a similar refractive index and extinction coefficient for the two reactors, although more subgap absorption is observed for the film deposited on the OpAL. This increase in absorption could be attributed to the increase in oxygen vacancies which is also seen in the XPS Mo3d peak in Figure 2.16(a). However, the O/Mo ratios found with RBS contradicts this observation. The films deposited on the OpAL reactor has a slightly higher band gap (2.89 eV versus 2.80 eV), and a slightly lower refractive index. The difference in refractive index can be explained by the difference in mass density (see Table 2.4).

As can be seen in Table 2.4, large amounts of C & N contamination were found with RBS in the films that were deposited on the OpAL. In addition, ERD measurements showed that the H content was 20 at.%, while the film deposited on the ALDii reactor contained 10 at.%. Although the GPC in terms of thickness increased by a factor of \( \sim 1.7 \), the number of deposited Mo at. nm\(^{-2}\) cycle\(^{-1}\) only increased by 8%. This can be explained by the incorporation of impurities, which also leads to a much lower density as compared to the film deposited on
the ALDii reactor. The higher level of impurities in the film can possibly be explained by the difference in plasma composition and in ion energy specifically. Due to a low pressure in the ALDii reactor, the ions have a high energy on the order of 30 eV, while in the OpAL reactor their energy is only a few eV. The high energy ions are more capable of removing the precursor ligands and thus might lead to lower impurity levels.

Table 2.4. Properties of MoO$_x$ films deposited at 100 °C on the OpAL and ALDii reactor, as determined from RBS, SE and XPS. The thickness of the films was approximately 20 nm. The number of deposited Mo at. nm$^{-2}$ cycle$^{-1}$ and chemical composition were determined from RBS, the refractive index and the Tauc band gap ($E_g$) from SE and the density from combining the RBS and SE results. Typical errors are indicated in the top row.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>GPC (Å)</th>
<th>Mo (at. nm$^{-2}$ cycle$^{-1}$)</th>
<th>O/Mo</th>
<th>[H] (at. %)</th>
<th>[C] (at. %)</th>
<th>[N] (at. %)</th>
<th>Mass density (g cm$^{-3}$)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OpAL</td>
<td>1.21 ± 0.04</td>
<td>1.53 ± 0.05</td>
<td>2.9 ± 0.1</td>
<td>20 ± 3</td>
<td>9 ± 4</td>
<td>8 ± 3</td>
<td>3.6 ± 0.3</td>
<td>2.89 ± 0.03</td>
</tr>
<tr>
<td>ALDii</td>
<td>0.72</td>
<td>1.42</td>
<td>2.8</td>
<td>10</td>
<td>&lt; 3</td>
<td>&lt; 2</td>
<td>4.3</td>
<td>2.80</td>
</tr>
</tbody>
</table>

After the self-limiting growth was confirmed for a deposition temperature of 100 °C, several depositions were carried out at higher deposition temperatures in order to check if the amorphous-crystalline transition could be reproduced on the OpAL reactor. Figure 2.17(a) shows the film thickness as a function of the number of ALD cycles, for deposition temperatures between 200 °C and 350 °C. Figure 2.17(b) shows the GPC as a function of cycles, which is found by determining the slope at different points on the curves in Figure 2.17(a). As can be seen an increase in GPC occurs during the deposition, similar to the results obtained on the ALDii reactor, which can be attributed to a transition from amorphous to crystalline growth. For deposition temperatures of 300 °C and 350 °C the GPC increases up to 1.7 Å and 2.8 Å, respectively. For a saturated ALD process this is an extremely high GPC, since normally a GPC on the order of 1 Å is found for ALD processes. Therefore more experiments are required to verify the saturating behavior and further study the growth at high temperatures.

Raman spectroscopy was done to verify the crystallinity of the films deposited at higher temperatures (see Figure 2.18). The films deposited at 300 °C and 350 °C indeed show peaks corresponding to the α crystal phase of MoO$_3$. For 250 °C two films with different thicknesses were deposited. As can be seen in Figure 2.18 the 10 nm thick film is amorphous, while the film with a thickness of 50 nm is clearly polycrystalline. This is consistent with the observation that the growth starts out as amorphous and evolves into polycrystalline growth as the thickness of the film increases, as was discussed in Section 2.3.1. Note that although crystalline growth was expected on the basis of the growth curves in Figure 2.17, it is somewhat surprising since a high impurity content can inhibit crystalline growth. For this reason, additional RBS measurements could be useful to check the contamination level for high deposition temperatures.
To conclude, slightly substoichiometric MoO$_x$ (x ≈ 2.9) was deposited on the OpAL reactor and saturating behavior was confirmed for a deposition of 100°C, with a GPC of 1.2 Å. As compared to the material deposited on the home-built reactor, the films have a lower density, due to a substantially higher impurity content. A transition from amorphous to polycrystalline was observed during film deposition for films deposited at temperatures between 250 °C and 350°C, in agreement with the measurements on the home-built reactor.
Chapter 3

ALD of MoO$_x$ for SHJ solar cells

**Abstract**: The potential of atomic-layer-deposited MoO$_x$ films for application as hole selective layers in silicon heterojunction (SHJ) solar cells has been investigated. High-purity MoO$_x$ films with a band gap of approximately 2.9 eV were deposited at a substrate temperature of 50 °C and were slightly substoichiometric with respect to MoO$_3$. Due to the high transparency of the MoO$_x$ optical simulations show a gain in short-circuit current density ($J_{sc}$) up to 1.0 mA/cm$^2$, as compared to the conventional SHJ cell with p-type a-Si:H. Lifetime measurements showed a promising implied open-circuit voltage ($V_{oc}$) of 710 mV for a stack of a-Si:H/MoO$_x$/In$_2$O$_3$:H and 718 mV for a a-Si:H/Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H stack, where 3 nm a-Si:H and $\sim$1 nm Al$_2$O$_3$ where used for passivation. The results demonstrate the compatibility of the novel ALD process with conventional a-Si:H and Al$_2$O$_3$ passivation schemes and are a promising step towards a more transparent front side of the SHJ solar cell.

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3.1. Introduction

In conventional silicon heterojunction (SHJ) solar cells a thin (≈10 nm) p-doped a-Si:H layer is used on the front side of the cell for the collection of holes created in the c-Si. However, due to the low band gap of a-Si (~1.7 eV) up to 5% of the incoming light is parasitically absorbed in this layer, limiting the efficiency of the cell. In order to prevent the parasitic absorption substantial research effort is focused on more transparent materials to replace the p-type a-Si:H, such as µc-SiO$_x$:H, a-SiO$_x$:H and a-SiC$_x$:H.

Recently Battaglia et al. introduced MoO$_x$ (x ≈ 3) as a promising candidate material, which has already been applied successfully as hole selective contact in organic and perovskite solar cells. The reason that MoO$_x$ makes a good option for the replacement of p-type a-Si:H as hole selective layer is its high transparency, which can lead to a significant reduction in parasitic absorption. As can be seen in Figure 3.1, MoO$_x$ has a much lower extinction coefficient and a higher band gap than a-Si:H (~3.0 eV versus 1.7 eV). In addition, the refractive index of MoO$_x$ is close to 2, which is ideal for light incoupling into the c-Si substrate. Although the mechanism of hole-selectivity of MoO$_x$ is still under debate, it is thought that the high work function of MoO$_x$ of around 6.6 eV plays an important role and leads to an electronic band diagram that is similar to the conventional SHJ solar cell. This will be further corroborated in Section 3.2.3 on the basis of equilibrium band diagram calculations.

![Figure 3.1. Refractive index n and extinction coefficient k of ALD MoO$_x$ and ICP deposited a-Si:H as determined by spectroscopic ellipsometry.](image)

Although Battaglia et al. showed an increase in $J_{sc}$ of 1.9 mA/cm$^2$ when replacing a-Si:H(p) by MoO$_x$, current-voltage (IV) measurements showed the presence of a barrier in the cells, leading to an efficiency of 18.8 % as opposed to 20.2 % for a reference cell with the standard p-type a-Si:H. However, temperature dependent measurements showed that the efficiencies of the two different cells are equal at an operating temperature of 70 °C, which is a realistic temperature for a PV module in the field. In this first study thermal evaporation was used for the deposition of the MoO$_x$, although this technique is not ideal for deposition of such thin layers due to the limited thickness control. A technique that is supposed to be more suited is atomic layer deposition (ALD), as was already suggested in the initial report by Battaglia. However, only few ALD processes for MoO$_x$ have been reported and existing processes are less...
suited for the application in PV, either due to impurity incorporation in the films or too high deposition temperatures, incompatible with thin a-Si:H layers.\textsuperscript{34–36}

Recently, we developed a new ALD process for the deposition of MoO\textsubscript{x} which uses (N\textsuperscript{t}Bu\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2})\textsubscript{2}Mo and O\textsubscript{2} plasma and yields excellent material properties for deposition temperatures down to 50 °C. Here, we explore the potential of this ALD process for the deposition of MoO\textsubscript{x} hole selective contacts for SHJ solar cells and will show it enables both a high level of passivation and excellent light incoupling into the c-Si wafer substrate. More specifically, stacks were prepared with either a-Si:H or ultrathin Al\textsubscript{2}O\textsubscript{3} (or a combination thereof) for passivation, MoO\textsubscript{x} as hole selective layer and In\textsubscript{2}O\textsubscript{3}:H as transparent conductive oxide (TCO). Firstly the mechanism for hole selectivity is discussed using simulated band diagrams for these stacks. Subsequently, the passivation performance of these stacks as a function of passivation layer thickness is assessed, in conjunction with optical simulations to determine the expected short-circuit current. Based on these results, the potential of ALD MoO\textsubscript{x} is put into perspective, and an outlook for further research is provided.

3.2. Experimental details

3.2.1. Film preparation

Low-resistivity (∼3-5 Ω cm) n-type float-zone Si(100) wafers (285 μm, double-side polished) were used as substrates for the different stacks. Prior to film deposition, the native oxide was removed by a one minute dip in dilute HF (1% in DI-H\textsubscript{2}O). Slightly substoichiometric molybdenum trioxide (MoO\textsubscript{3}) was deposited at 50 °C using (N\textsuperscript{t}Bu\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2})\textsubscript{2}Mo as Mo precursor and O\textsubscript{2} plasma as oxidant in a home-built ALD reactor. The details of this ALD process have been addressed in Chapter 2. To minimize the plasma-induced damage to the passivating a-Si:H and Al\textsubscript{2}O\textsubscript{3} layers, the MoO\textsubscript{x} was deposited using milder plasma conditions, i.e. 48 W, 7.5 mTorr chamber pressure and 2 s plasma exposure, which still resulted in good material properties. In comparison, the standard MoO\textsubscript{x} recipe uses 100 W, 5.1 mTorr and 4 s plasma exposure. Intrinsic a-Si:H depositions were performed at 50 °C by inductively coupled plasma chemical vapour deposition (ICP-CVD) in an Oxford Instruments PlasmalabSystem100 ICP 180 from pure SiH\textsubscript{4}. Al\textsubscript{2}O\textsubscript{3} passivation layers were deposited in an Oxford Instruments OpAL\textsuperscript{TM} ALD reactor at 200 °C using trimethylaluminum (TMA) and O\textsubscript{2} plasma.\textsuperscript{48} To activate the surface passivation the films were post-annealed in an inert N\textsubscript{2} atmosphere. For a-Si:H this was done at 300 °C for 30 s, whereas the Al\textsubscript{2}O\textsubscript{3} passivation layers were annealed at 400 °C for 1 minute. When a combination of a-Si:H and Al\textsubscript{2}O\textsubscript{3} was used the anneal was done at 300 °C for 30 s to prevent damage to the a-Si:H, which is sensitive to high temperatures. Layers of approximately 75 nm of In\textsubscript{2}O\textsubscript{3}:H were deposited by thermal ALD using cyclopentadienyl indium (InCp) and a combination of H\textsubscript{2}O and O\textsubscript{2} at 100 °C in the OpAL\textsuperscript{TM} reactor. This process yields amorphous In\textsubscript{2}O\textsubscript{3}:H (a-In\textsubscript{2}O\textsubscript{3}:H), which is subsequently annealed in an inert N\textsubscript{2} atmosphere at 200 °C to crystallize the film. Crystallization of the In\textsubscript{2}O\textsubscript{3}:H is done to obtain excellent film properties, i.e. a very high mobility of 138 cm\textsuperscript{2}/Vs, a carrier density of 1.8×10\textsuperscript{20} cm\textsuperscript{-3} and a resistivity of 0.27 mΩ cm.\textsuperscript{16} It was confirmed that this anneal step does not affect the crystallinity of the MoO\textsubscript{x}, Al\textsubscript{2}O\textsubscript{3} and a-Si:H films, although it can have other effects on the material properties as will be discussed later in Section 3.3.2.
In particular three different stacks were deposited to study the potential of the ALD MoO$_x$ films for SHJ solar cells, which can be seen in Figure 3.2. Type I consisted of a-Si:H/MoO$_x$/In$_2$O$_3$:H and resembled the conventional SHJ solar cell the most, having a MoO$_x$ instead of p-type a-Si:H hole selective layer. The second type was an Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H stack, where the Al$_2$O$_3$ served as passivation layer instead of a-Si:H. Al$_2$O$_3$ would be preferable as passivation layer, since Al$_2$O$_3$ has a much lower absorption coefficient and higher band gap (6.8 eV versus 1.7 eV) and therefore leads to minimal parasitic absorption. Note that Al$_2$O$_3$ has been extensively used for the passivation of c-Si.$^{42,43}$ Considering that Al$_2$O$_3$ is a dielectric and forms a barrier through which the holes have to tunnel, the layer was kept very thin (~1 nm). Since for such thin layers the thickness of the layer cannot be accurately measured, the amount of ALD cycles instead of the thickness was used as variable.

It should be noted that due to its negative charge density Al$_2$O$_3$ can induce field effect passivation in addition to the chemical passivation it provides. This is in contrast with a-Si:H which only leads to chemical passivation, where dangling bonds on the c-Si surface are passivated by H present in the a-Si:H layer. Moreover, the negative charge in Al$_2$O$_3$ is beneficial for the collection of holes (see Section 3.3.1). In order to achieve outstanding passivation and excellent transparency, the two materials were also combined in a stack of a-Si:H/Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H (Type III).

For Type I and Type II the thicknesses of the a-Si:H and Al$_2$O$_3$ were varied, in order to study the dependence of the level of passivation on the thickness. For Type III just one stack was deposited, consisting of 3 nm a-Si:H and 9 cycles Al$_2$O$_3$ (~1 nm). To passivate the backside of the c-Si wafer layers of 10 nm a-Si:H and 15 nm Al$_2$O$_3$ were used for Type I and Type II, respectively. A 10 nm a-Si:H layer was used for stack Type III, in analogy to Type I. Both passivation layers result in a $iV_{oc}$ well above 700 mV when deposited on both sides of the c-Si, meaning they do not limit the $iV_{oc}$ of stacks I, II and III.

![Figure 3.2](image_url)  
**Figure 3.2.** Different types of passivating stacks that were used for lifetime measurements and optical simulations. The layers are not drawn to scale.
3.2. Experimental details

3.2.2. Film analysis

Variable-angle spectroscopic ellipsometry was done \textit{ex situ} to assess the optical properties of the films using a J.A. Woollam Inc. M2000D ellipsometer (1.25 - 6.5 eV). For MoO$_x$, a Tauc-Lorentz oscillator in combination with a Gaussian oscillator was used, while for a-Si:H a Cody-Lorentz oscillator was used. The passivation quality of the different film stacks was quantified by the implied open-circuit voltage ($iV_{oc}$) obtained from minority carrier lifetime measurements using a Sinton WCT-120TS in the generalized mode.$^{103}$ This diagnostic uses the change in photoconductivity upon illumination with a short light flash to measure both the effective minority carrier lifetime ($\tau_{eff}$) and the $iV_{oc}$. The optical constants of the different stacks, needed for the correct determination of the $iV_{oc}$ from the Sinton measurements, were calculated using the $J_{sc}$ as obtained from optical simulations. An additional discussion on lifetime measurements can be found in the Supplementary Info, Section 3.A. Transmission electron microscopy (TEM) was carried out using a JEM-ARM200F microscope from JEOL.

3.2.3. Band diagram modeling & optical simulations

For the equilibrium band diagram calculations the Poisson-Boltzmann equation was solved in COMSOL.$^*$ The approximation of Aymerich-Humet was used for a numerical approximation of the Fermi Dirac integral.$^{104}$ Material properties, such as carrier density and electron affinity, that were used for the simulations can be found in the Supplementary Info, Section 3.B.

Optical modeling of the short-circuit current density $J_{sc}$ of different solar cell structures was done using the online optical calculator OPAL 2.$^{105}$ To calculate the ($J_{sc}$) of a specific solar cell in OPAL 2, the different films on the front side of the cell are defined, in addition to the wafer substrate. For each separate film the thickness and optical constants have to be specified. In addition, the surface morphology and incident light source are selected. Using the provided information, OPAL 2 calculates the photon currents that are reflected and absorbed in the stack of thin films and the c-Si substrate by ray tracing using the light trapping model of Green.$^{106}$ For the calculation of the $J_{sc}$ it is assumed that all photons reaching the c-Si wafer will be absorbed in the c-Si, i.e. a collection efficiency of 1, which corresponds to a generated current of 44 mA/cm$^2$. Furthermore, it is assumed that photons absorbed in the front layers do not contribute to the $J_{sc}$. This is generally true for the TCO and doped a-Si:H layers. However, for the intrinsic a-Si:H layer in a standard SHJ solar cell the collection efficiency can be around 30%.$^{97}$ It should also be noted that the simulation yields the active-area short-circuit current density, i.e. shading by the metal contacts is not taken into account.

For the simulations used in this work, the optical constants of the MoO$_x$, In$_2$O$_3$:H and Al$_2$O$_3$ were taken from spectroscopic ellipsometry measurements, while for intrinsic and doped a-Si:H the optical constants from Holman \textit{et al}, provided in the database of OPAL 2, were used.$^{97}$ Moreover, a surface of random upright pyramids and a normally incident AM1.5g spectrum, standard for solar cell characterization, were selected. The optical constants that were used for MoO$_x$ and a-Si:H can be seen in Figure 3.1 and Figure 3.10 (Supplementary Info, Section 3.B) shows the optical constants of In$_2$O$_3$:H and Al$_2$O$_3$.

*$^*$Sjoerd Smit is gratefully acknowledged for supplying the COMSOL model and assistance with the calculations.
3.3. Results and discussion

3.3.1. Band diagram modeling

Although the exact mechanism of hole extraction is not fully understood yet, it is thought that both the defect states and the work function of MoO$_x$ play an important role$^{20,102}$ In order to get a better understanding of the working mechanism of the hole selectivity, equilibrium calculations of the band diagram were done. In Figure 3.3 the calculated band diagrams of a conventional SHJ cell and two different SHJ cells with MoO$_x$ are shown. The band diagram of a cell with the conventional p-type a-Si:H can be seen in Figure 3.3(a), while Figure 3.3(b) corresponds to a cell with MoO$_x$ as selective layer and a-Si:H(i) as passivation layer. In addition, Figure 3.3(c) shows the band diagram for a cell with a MoO$_x$ selective layer and an Al$_2$O$_3$ passivation layer. For the p-type a-Si:H layer a thickness of 10 nm was used, while the MoO$_x$ layer was 5 nm thick. The thickness of the a-Si:H(i) and Al$_2$O$_3$ passivation layers were 5 nm and 1 nm, respectively. A typical value of $-5.2 \times 10^{12}$ cm$^{-3}$ was taken for the fixed charge ($Q_f$) at the c-Si/Al$_2$O$_3$ interface.$^{107}$ Additional material parameters used for the calculation can be found in the Supplementary Info, Section 3.B. As can be seen in Figure 3.3(b) and (c), the MoO$_x$ layer induces upward band bending in the c-Si, similar to the case of an a-Si:H(p) hole selective layer in Figure 3.3(a). This upwards band bending leads to a barrier for the electrons, while it induces the extraction of holes towards the a-Si:H(i) or Al$_2$O$_3$ layer.

Even though a-Si:H(p) and MoO$_x$ lead to a similar band bending in the c-Si, the working principle is considerably different. While the doping in the p-type a-Si:H induces the band bending for the conventional cell, it is the high work function of the MoO$_x$ that is responsible in the other case. The simulations confirmed that a lower work function for MoO$_x$ induces less band bending, indicating that a certain work function is required to achieve sufficient selectivity for the holes.

Another important difference is that a-Si:H is a p-type material, while MoO$_x$ is an n-type material, which causes the desired electron-hole recombination to occur at a different interface in the solar cell, as can be seen in Figure 3.3. Note that for a current to flow through the solar cell, electrons and holes should recombine somewhere in the cell, after they have been extracted in opposite directions from the c-Si by the hole selective layers. In the conventional SHJ solar cell holes cross the barrier caused by the valence band offset at the c-Si/a-Si:H(i) interface by tunnel-hopping through the tail states in the a-Si:H(i).$^{20,108,109}$ The holes subsequently recombine with electrons in the valence band at the interface between the p-type a-Si:H and TCO, as is shown in Figure 3.3(a). This is in contrast to the cells with MoO$_x$, where the recombination takes place at the interface between the MoO$_x$ and the passivation layer. For the cell with a-Si:H passivation in Figure 3.3(b), the holes transit through the tail states in the a-Si:H, whereas the holes have to tunnel through the barrier formed by the Al$_2$O$_3$ in Figure 3.3(c). As said before, the Al$_2$O$_3$ layer should be thin in order to achieve a sufficient tunnel current. After the holes reach the MoO$_x$ surface they can transiting through the defect states in the MoO$_x$ and recombine with the electrons in the valence band. Note that the defect states have not been included in the COMSOL model, since the exact nature of the defects is unclear.
3.3. Results and discussion

Although the recombination occurs in the same place for the cells in Figure 3.3(b) and (c), a significant difference between the two structures is the presence of negative fixed charge at the c-Si/Al$_2$O$_3$ interface, which induces additional band bending. However, due to the already significant band bending caused by the MoO$_x$, the typical $Q_f$ of $-5 \times 10^{12}$ only induces a relatively small additional band bending of 0.04 eV, as compared to a $Q_f$ of zero.

![Figure 3.3](image)

**Figure 3.3.** Calculated equilibrium band diagrams of SHJ solar cells with (a) 10 nm a-Si:H(p) and (b) & (c) 5 nm MoO$_x$ as hole selective layer. In the (b) 5 nm a-Si:H(i) is used as passivation layer, while cell (c) contains 1 nm of Al$_2$O$_3$ for passivation.

### 3.3.2. Passivation studies & optical simulations

Prior to the passivation studies and optical simulations, a stack of Type I was studied using a cross sectional TEM image (see Figure 3.4). A sharp interface can be seen between the ICP CVD deposited a-Si:H passivation layer and the c-Si wafer, which is a prerequisite for good surface passivation.$^{110}$ Moreover, the image shows that the novel ALD process can be used for the deposition of a very thin, uniform MoO$_x$ layer. Upon close inspection of the a-Si:H layer it can be seen there is some contrasts difference approximately halfway through the layer. This is an indication of intermixing of the MoO$_x$ and a-Si:H layers, which could have taken...
place during deposition, crystallization of the In$_2$O$_3$:H at 200 °C or maybe during the TEM lamella preparation by the focused ion beam (FIB). Further study is needed to confirm this and to determine how this would affect solar cell operation. On top of the MoO$_x$ the crystallized In$_2$O$_3$:H can be seen, which has a defect-free crystal structure, in agreement with observations by Macco et al.$^{16}$

![Figure 3.4. High resolution cross-sectional TEM image showing the passivating a-Si:H/MoO$_x$/In$_2$O$_3$:H stack on c-Si.](image)

After it was verified that the novel ALD process enables the deposition of thin, conformal layers in SHJ structures, the anticipated gain in $J_{sc}$ was calculated by optical simulations in OPAL 2. Using the optical constants of Figure 3.1 and assuming a MoO$_x$ thickness of 5 nm, a $J_{sc}$ of 41.7 mA/cm$^2$ is found. Even if 10 nm instead of 5 nm MoO$_x$ would be needed to achieve an acceptable level of selectivity, the $J_{sc}$ would remain 41.7 mA/cm$^2$, due to the extremely low absorption coefficient in the solar spectrum range (< 4.0 eV). In comparison, putting in the structure of a conventional SHJ cell with 10 nm a-Si:H(p) as selective layer results in a $J_{sc}$ of 40.7 mA/cm$^2$. Note that the incoming solar spectrum provides a photon current of 44.0 mA/cm$^2$, meaning that 2.3 mA/cm$^2$ (5.2%) and 3.3 mA/cm$^2$ (7.5%) are lost due to the front sides with MoO$_x$ and a-Si:H(p), respectively. However, the MoO$_x$ thickness should be kept as thin as possible, in order to minimize the presence of a barrier in the cell, while still achieving enough selectivity, as was also suggested by Battaglia.$^{20}$

**Type I: a-Si:H/MoO$_x$/In$_2$O$_3$:H**

Since it is expected that both the $J_{sc}$ and the level of passivation, quantified by the $\tau_{eff}$ and the $iV_{oc}$, depend strongly on the thickness of the a-Si:H passivation layer, several stacks of Type I were made with the a-Si:H thickness varying between 3 nm and 9 nm. Figure 3.5(a) shows the measured minority carrier lifetime $\tau_{eff}$ for the different process steps of a stack with 3 nm a-Si:H. As can be seen the a-Si:H layer provides excellent passivation after a post-anneal at 300 °C for 30 s. After the MoO$_x$ deposition the lifetime is dramatically lower, accompanied by a
3.3. Results and discussion

decrease in \( iV_{oc} \) from 691 mV to 650 mV. This decrease in \( iV_{oc} \) is attributed to plasma-induced damage occurring during the MoO\(_x\) deposition and has been reported before for plasma-based deposition processes.\(^{96,111}\) After the deposition of the amorphous In\(_2\)O\(_3\):H TCO the passivation is slightly recovered, caused by the unintentional anneal step occurring during the In\(_2\)O\(_3\):H deposition at 100 °C, which takes roughly 4.5 hours. It is known that the passivation can be (partly) recovered after plasma-induced damage by annealing, due to changes in the microstructure of the material.\(^{111}\) After the In\(_2\)O\(_3\):H is crystallized at 200 °C the passivation is completely recovered and even slightly improved, as is evidenced by a \( \tau_{eff} \) of 0.9 ms (at a carrier density of \( 1 \times 10^{15} \) cm\(^{-3} \)), as compared to a lifetime of 0.8 ms for the initial a-Si:H passivation. This improvement in passivation is again attributed to the effect of the anneal step on the microstructure. Note that additional stacks were deposited which received the first anneal step at 300 °C after the MoO\(_x\) deposition, resulting in much lower values for \( iV_{oc} \). Therefore the first anneal step right after the a-Si:H deposition is necessary to achieve good passivation. Although the plasma-induced damage is a drawback of the MoO\(_x\) deposition process, the final lifetime of 920 ms and implied \( V_{oc} \) of 710 mV demonstrate the potential of the novel MoO\(_x\) ALD process for implementation in SHJ solar cells.

In Figure 3.5(b) the \( iV_{oc} \), measured with the Sinton lifetime technique, and the \( J_{sc} \), obtained from OPAL 2 simulations, are given as a function a-Si:H thickness. The results show that already with an a-Si:H layer of just 3 nm an excellent level of passivation can be achieved (\( iV_{oc} > 700 \) mV) prior to MoO\(_x\) deposition. Moreover, the \( iV_{oc} \) increases slightly with a-Si:H thickness, while at the same time the \( J_{sc} \) of the cell decreases with increasing a-Si:H thickness, as a consequence of the parasitic absorption. Therefore, a trade-off is to be made between the passivation and the short-circuit current density \( J_{sc} \), which both directly affect the efficiency of a solar cell.

![Figure 3.5](image)

**Figure 3.5.** (a) Injection-dependent minority carrier lifetime measurements for a stack of a-Si:H/MoO\(_x\)/In\(_2\)O\(_3\):H, after each processing step. The a-Si:H thickness was 3 nm. The (orange) squares indicate the implied \( V_{oc} \) under 1 sun illumination. (a) Implied \( V_{oc} \) under 1 sun illumination for a stack of a-Si:H/MoO\(_x\)/In\(_2\)O\(_3\):H as a function of a-Si:H thickness, after each processing step. On the right axis the short-circuit current density \( J_{sc} \) is shown. The lines serve as a guide to the eye.
Type II: Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H

In order to further reduce the parasitic absorption caused by the a-Si:H, the intrinsic a-Si:H passivation layer was replaced by Al$_2$O$_3$, which has a much lower absorption coefficient. Calculation of the Type II stack in the OPAL 2 simulator showed a promising $J_{sc}$ of 42.7 mA/cm$^2$ for a stack with a 1 nm thick Al$_2$O$_3$ layer. Note that due to the high transparency of Al$_2$O$_3$ the $J_{sc}$ is constant for thicknesses between 0 nm and 2 nm, although the $iV_{oc}$ does depend on the thickness of the passivation layer. Moreover, since Al$_2$O$_3$ is a dielectric it forms a barrier in a solar cell and the contact resistance of the cell increases with Al$_2$O$_3$ thickness. Therefore the thickness should be kept as low as possible, while achieving a reasonable level of passivation. Previous work on Al$_2$O$_3$/ZnO stacks showed that an Al$_2$O$_3$ layer in the range of 1 nm (~9 ALD cycles) still results in an acceptable tunnel current.$^{112,113}$ However, measurements of the contact resistance should be performed in order to confirm this for the type of stack used in this work.

Figure 3.6(a) shows minority lifetime curves for a stack with 9 cycles Al$_2$O$_3$. Similar to stacks of Type I, a dramatic decrease in $iV_{oc}$ and lifetime was observed after the deposition of the MoO$_x$, which is almost completely recovered after the crystallization of the In$_2$O$_3$:H at 200 °C. The decrease in lifetime is due to a modification of the microstructure of the Al$_2$O$_3$ upon plasma-exposure, which can be partly or sometimes completely reversed by an anneal step.$^{96}$ For stacks of Type II it was confirmed that annealing the Al$_2$O$_3$ layer prior to MoO$_x$ deposition is needed for good passivation, as was also the case for the a-Si:H layer in Type I. In Figure 3.6 (b) the $iV_{oc}$ is shown as a function of the number of Al$_2$O$_3$ ALD cycles. As expected, the $iV_{oc}$ increases with Al$_2$O$_3$ thickness and reaches a value of 690 mV for 13 ALD cycles after crystallization of the In$_2$O$_3$:H. However, it is expected that 13 ALD cycles leads to a too high contact resistance, while 9 cycles is thought to be acceptable and still results in a reasonable $iV_{oc}$ of 672 mV.

![Minority carrier lifetime vs. density](image)

![Implied $V_{oc}$ vs. ALD cycles](image)

**Figure 3.6.** (a) Injection-dependent minority carrier lifetime for a stack of Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H, after each processing step. The (orange) squares indicate the implied $V_{oc}$ under 1 sun illumination. 9 ALD cycles were performed for the deposition of the Al$_2$O$_3$ layer. (b) Implied $V_{oc}$ under 1 sun illumination for a stack of Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H as a function of Al$_2$O$_3$ ALD cycles, after each processing step.
3.3. Results and discussion

By comparing Figure 3.6 with Figure 3.5 it can be concluded that in terms of $iV_{oc}$ Type II performs worse than Type I. However, the high $J_{sc}$ of 42.7 mA/cm$^2$, compared to the $J_{sc}$ of 42.1 mA/cm$^2$ for the stack that employs a-Si:H for passivation, is a big advantage. Therefore a front side of Type II could be preferable if the $iV_{oc}$ could be further improved, for instance by optimizing the MoO$_x$ or Al$_2$O$_3$ deposition process and subsequent anneal steps.

**Type III: a-Si:H/Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H**

By combining a-Si:H and Al$_2$O$_3$ for the passivation of the c-Si it was expected that the best possible $iV_{oc}$ could be achieved, while simultaneously profiting from excellent transparency. As stated earlier, in such a stack the Al$_2$O$_3$ can induce additional selectivity and simultaneously improve the passivation. A thickness of 3 nm a-Si:H and 9 ALD cycles of Al$_2$O$_3$ were used, for which an estimated $J_{sc}$ of 42.1 mA/cm$^2$ was found using the OPAL 2 calculator.

![Minority carrier lifetime](image.png)

**Figure 3.7.** Injection-dependent minority carrier lifetime for a stack of a-Si:H/Al$_2$O$_3$/MoO$_x$/In$_2$O$_3$:H, after each processing step. The (orange) squares indicate the implied $V_{oc}$ under 1 sun illumination. The a-Si:H thickness was 3 nm and 9 Al$_2$O$_3$ ALD cycles (~1 nm) were performed.

From the lifetime curves in Figure 3.7 it can be seen that the stack indeed results in excellent passivation, with a $iV_{oc}$ of 718 mV for the final stack. After the In$_2$O$_3$:H crystallization the carrier lifetime is higher than after the initial a-Si:H + Al$_2$O$_3$ passivation. This is expected to be due to the fact that the initial anneal step of 300 °C for 30 s is not ideal for the Al$_2$O$_3$, i.e. the Al$_2$O$_3$ actually requires a higher anneal temperature or longer anneal time to achieve the optimal level of passivation. Therefore the quality of the Al$_2$O$_3$ layer is improved during the In$_2$O$_3$:H crystallization step, as compared to after the initial anneal step. Note that annealing at a higher temperatures would lead to damage to the a-Si:H layer. However, optimization of the different anneal steps could possibly result in a further enhancement of the $iV_{oc}$. 

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3.4. Conclusion

The potential of a novel ALD process using \((\text{N}^\text{t} \text{Bu})_2(\text{NMe}_2)_2\text{Mo}\) and \(\text{O}_2\) plasma for the deposition of MoO\(_x\) hole selective layers was demonstrated. Overall, the results show that the novel ALD process enables the deposition of MoO\(_x\) in application-relevant test structures, achieving both a good level of passivation and an improved \(J_{sc}\), as compared to a SHJ structure with p-type a-Si:H. Although the plasma-induced damage is a downside of the MoO\(_x\) ALD process, the passivation level is fortunately recovered to a great extent after post-annealing.

Using optical simulations it was shown that a \(J_{sc}\) of 41.7 mA/cm\(^2\) could be obtained in a SHJ with a 5 nm thick MoO\(_x\) hole selective layer, compared to a \(J_{sc}\) of 40.7 mA/cm\(^2\) for a conventional SHJ cell with 10 nm p-type a-Si:H. An excellent level of passivation \((iV_{oc} = 718\, \text{mV})\) was achieved with a stack of Type III, consisting of just 3 nm a-Si:H and 9 cycles Al\(_2\)O\(_3\). However, the need of an extra processing step could be a limiting factor for the implementation of such a structure in industry.

To make a proper comparison between the different stacks prepared in this work, the results from the lifetime measurements and the optical simulations were used for the estimation of the achievable active area efficiency \((\eta)\) of solar cells with the three different front sides (See Table 3.1). A fill factor of 80% was assumed for this calculation, which is of course a crude assumption, but is reasonable for present-day SHJ solar cells.\(^{10}\) As can be seen in Table 3.1 Type III shows the highest efficiency (24.2%), due to the combination of a high \(iV_{oc}\) and \(J_{sc}\). In order to achieve an even higher \(J_{sc}\) maybe a thinner intrinsic a-Si:H layer could be deposited while still achieving sufficient passivation. Moreover, an optimization of the different anneal steps could contribute to an improved \(iV_{oc}\) and thus enhanced efficiency. Note that the two different stacks of Type I shown in Table 3.1 have different a-Si:H thicknesses, but result in the same efficiency, which is due to the trade-off between \(J_{sc}\) and \(iV_{oc}\).

Table 3.1. \(iV_{oc}\), \(J_{sc}\) and estimated active area efficiency \((\eta)\) obtained for the three different stack types used in this study. Stack Type I consisted of a-Si:H/MoO\(_x\)/In\(_2\)O\(_3\):H, Type II of Al\(_2\)O\(_3\)/MoO\(_x\)/In\(_2\)O\(_3\):H and Type III of a-Si:H/Al\(_2\)O\(_3\)/MoO\(_x\)/In\(_2\)O\(_3\):H. The MoO\(_x\) and In\(_2\)O\(_3\):H thicknesses were kept constant at 5 nm and 75 nm, respectively.

<table>
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<th>(iV_{oc}) (mV)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>(\eta) (%)</th>
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</tbody>
</table>
Although the results obtained in this study are very promising, it should be noted they are only a first indication and that the hole selectivity of the ALD MoO$_x$ layer has not yet been confirmed. As the band diagram calculations confirmed, the selectivity is affected by the work function of the MoO$_x$ layer. Therefore the hole selectivity should be confirmed, either by measuring the band bending using surface photovoltage spectroscopy (SPV) or by making actual solar cell devices, of which the hole selectivity can be checked by Suns-V$_{oc}$ measurements.\textsuperscript{114,115} In addition to the verification of the hole selectivity, the contact resistance of stacks of Type II and III should be measured using the transmission line model (TLM) technique.\textsuperscript{116} As was explained, the insertion of an Al$_2$O$_3$ layer can lead to a barrier in the cell. However, based on previous work it is expected that 9 ALD cycles (~1 nm) would still result in an acceptable tunnel current and thus $J_{sc}$.\textsuperscript{112}
Usually the performance of a solar cell is characterized by its efficiency, which is given by:

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}}$$  \hspace{1cm} (3.1)$$

where $V_{oc}$ is the open-circuit voltage, $J_{sc}$ the short-circuit current, $FF$ the fill factor and $P_{in}$ the power of the incoming light. However, to calculate this efficiency a complete solar cell needs to be made and the illuminated current-voltage (IV) curve needs to be measured. As will be addressed in this Chapter, several other techniques can be employed in order to characterize a solar cell structure without needing to fabricate a complete cell. Firstly, Section 3.A will describe how the Sinton method can be used to measure the effective minority carrier lifetime $\tau_{eff}$ and implied $V_{oc}$.\textsuperscript{103, 117} Note that $\tau_{eff}$ is a measure for the rate at which the minority carriers recombine after being created in the c-Si. Additionally, the $J_{sc}$ of a solar cell can be estimated by performing optical simulations, as will be discussed in Section 3.B. Band diagram calculations can be done using available software packages such as AFORS HET, or by using a custom computer model, which is done in this study.\textsuperscript{118} Lastly, once a solar cell structure is completed up to the point that only the metal contacts need to be added, a Suns-$V_{oc}$ measurement can be done to measure the actual $V_{oc}$, which will be shown in Section 3.D.

### 3.A. Sinton lifetime measurements

The Sinton lifetime method can be used to measure the minority carrier lifetime and the so-called implied $V_{oc}$ ($iV_{oc}$). The principle of this method is based on the change in photoconductance of a sample upon illumination with a flash lamp. By measuring the change in photoconductance $\sigma_L$ the minority carrier lifetime $\tau_{eff}$ can be calculated according to:

$$\tau_{eff} = \frac{\sigma_L}{J_{ph}(\mu_n + \mu_p)}$$  \hspace{1cm} (3.2)$$

Here, $J_{ph}$ is the photo generated current, which can be calculated using an optical simulator (see also Section 3.B). $\mu_n$ and $\mu_p$ are the electron and hole mobility, respectively, which depend on the carrier density and are well known for c-Si. Moreover, for a c-Si wafer which is reasonably well passivated on both sides, the measured $\sigma_L$ can be used to calculate the excess
minority carrier density $\Delta n$ given by:

$$\Delta n = \frac{\sigma_L}{qW(\mu_n + \mu_p)}$$  \hspace{1cm} (3.3)$$

where $q$ is the elementary charge and $W$ is the thickness of the wafer substrate. Using $\Delta n$ obtained from Equation 3.3 the implied $V_{oc}$ can then be calculated according to:

$$iV_{oc} = \frac{kT}{q} \ln \left( \frac{(N_D + \Delta n)\Delta n}{n_i^2} \right)$$  \hspace{1cm} (3.4)$$

Here, $kT/q$ is the thermal voltage, $N_D$ is the dopant density of the wafer and $n_i$ is the intrinsic carrier concentration. Standard procedure is to report the $iV_{oc}$ for an illumination of 1 sun, which is possible since $\sigma_L$ is measured as a function of the light intensity. As said, the measured $iV_{oc}$ can be used to characterize a solar cell structure without needing to fabricate a full cell and measure the $V_{oc}$. However, it should be realized that the measured $iV_{oc}$ is not the same as the $V_{oc}$, as is shown in Figure 3.8. The $iV_{oc}$ is a measurement of the quasi Fermi level splitting in the c-Si, while the actual $V_{oc}$ is the voltage difference between the front and the backside of the solar cell. As a consequence of this, a good level of passivation is sufficient for measuring a high $iV_{oc}$, while good selectivity for the holes and electrons is additionally required for obtaining a high $V_{oc}$. As can be seen, bending of the quasi Fermi level at the surface can cause a difference of $\Delta V_{oc}$ between the actual $V_{oc}$ and the implied $V_{oc}$, meaning that the actual $V_{oc}$ is always equal or lower than the implied $V_{oc}$. However, typically the difference is relatively small, and $iV_{oc}$ can be used as a good estimation for the characterization of a solar cell.

![Figure 3.8. Schematic band diagram of a SHJ solar cell, indicating the difference between the implied $V_{oc}$ and the actual or external $V_{oc}$. $E_{F,n}$ and $E_{F,p}$ indicate the quasi Fermi levels for the electrons and holes, respectively. (This figure has been adapted from Bivour et al.\textsuperscript{115})](image-url)
3.B. Optical simulations

In addition to the estimation of the $V_{oc}$, a solar cell structure can be characterized by estimating the $J_{sc}$ using optical simulations. Although there are several optical simulators available, the OPAL 2 simulator from PV lighthouse was used in this study.* As was explained in Section 3.2.3 this simulator is operated by defining the stack of films which make up the front side of the cell. For each film the thickness, the refractive index $n$, and the extinction coefficient $k$ are specified, which can either be found in the OPAL 2 database, or uploaded from a data file. It should be mentioned that the refractive index $n$ and the extinction coefficient $k$ of the ALD MoO$_x$ developed in this work have recently been added to the database of the OPAL 2 optical simulator by the developers, enabling others to use the constants for their calculations. Using the provided solar cell structure OPAL 2 calculates the photon currents that are reflected and absorbed in the stack of thin films and the c-Si substrate by ray tracing. A screenshot of the interface of the simulator can be seen in Figure 3.9.

![Screenshot of the OPAL 2 optical simulator](image)

**Figure 3.9.** Screenshot of the OPAL 2 optical simulator which is used for the estimation of the $J_{sc}$ of different solar cell structures. The complete front side of the cell is specified, including the optical constants and the thicknesses.

The refractive index $n$ and the extinction coefficient $k$ of c-In$_2$O$_3$:H and Al$_2$O$_3$ that were used for the simulations are given in Figure 3.10. Note that the $n$ and $k$ for a-Si:H and MoO$_x$ are shown in Figure 3.1. The dielectric function of the c-In$_2$O$_3$:H was parameterized with a Tauc-Lorentz oscillator and an additional Drude oscillator, which accounts for free carrier absorption at low photon energy. As can be seen in Figure 3.10 the c-In$_2$O$_3$:H is highly transparent, having a band gap of around 3.3 eV, and very low absorption at low photon energy. For Al$_2$O$_3$ a Cauchy model was used. Al$_2$O$_3$ has a very high band gap (~6.8 eV) and a very low extinction coefficient, making it ideal for use as passivation layer in a SHJ solar cell.

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*Available at www.pvlighthouse.com.au
3.C. Band diagram modeling

To get a better understanding of the hole selective mechanism in different types of SHJ solar cells, equilibrium band diagrams were calculated using a COMSOL model (see Section 3.3.1). The material properties used for these calculations are given in Table 3.2.

Table 3.2. Material properties used for the equilibrium calculation of the band diagrams. \( \varepsilon_r \) is the dielectric constant, \( N_D \) the dopant density and \( N_V \) and \( N_C \) are the densities of states in the valence and conduction band, respectively. Moreover, \( \chi \) is the electron affinity, \( E_g \) the band gap and \( Q_f \) the fixed charge density. The negative dopant density of a-Si:H(p) indicates the p-type nature of the material.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \varepsilon_r )</th>
<th>( N_D ) (cm(^{-3}))</th>
<th>( N_C ) (cm(^{-3}))</th>
<th>( N_V ) (cm(^{-3}))</th>
<th>( \chi ) (eV)</th>
<th>( E_g ) (eV)</th>
<th>( Q_f ) (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si(n)</td>
<td>11.9</td>
<td>1.6 \times 10^{15}</td>
<td>2.85 \times 10^{19}</td>
<td>2.69 \times 10^{19}</td>
<td>4.05</td>
<td>1.12</td>
<td>0</td>
</tr>
<tr>
<td>a-Si:H(i)</td>
<td>11.9</td>
<td>0</td>
<td>1.00 \times 10^{20}</td>
<td>1.00 \times 10^{20}</td>
<td>3.9</td>
<td>1.7</td>
<td>0</td>
</tr>
<tr>
<td>a-Si:H(p)</td>
<td>11.9</td>
<td>-1.0 \times 10^{19}</td>
<td>1.00 \times 10^{20}</td>
<td>1.00 \times 10^{20}</td>
<td>3.9</td>
<td>1.7</td>
<td>0</td>
</tr>
<tr>
<td>MoO(_x)</td>
<td>18.0</td>
<td>3.0 \times 10^{16}</td>
<td>1.00 \times 10^{20}</td>
<td>1.00 \times 10^{20}</td>
<td>5.7</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>6.0</td>
<td>0</td>
<td>1.00 \times 10^{20}</td>
<td>1.00 \times 10^{20}</td>
<td>2.05</td>
<td>6.8</td>
<td>-5 \times 10^{12}</td>
</tr>
<tr>
<td>c-In(_2)O(_3):H</td>
<td>8.9</td>
<td>1.8 \times 10^{16}</td>
<td>2.50 \times 10^{20}</td>
<td>2.50 \times 10^{20}</td>
<td>5.0</td>
<td>3.3</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 3.10. Refractive index \( n \) and extinction coefficient \( k \) of ALD Al\(_2\)O\(_3\) and c-In\(_2\)O\(_3\):H as determined from spectroscopic ellipsometry.
3.D. Initial results on OpAL™ reactor

As was discussed in Section 2.E, the MoO₃ ALD process has also been developed on the OpAL reactor for a deposition temperature of 100 °C to enable the direct deposition of the In₂O₃:H TCO on the MoO₃ layer, without breaking the vacuum. In order to check the compatibility of the process on this reactor with the SHJ technology, a passivating stack similar to the ones discussed in Section 3.3.2 was made and the carrier lifetime was measured. For this first test, a stack was deposited with 5 nm a-Si:H(i) for passivation, 5 nm MoOₓ as hole selective layer and 75 nm In₂O₃:H TCO. The MoOₓ selective layer was deposited at 100 °C, after which the a-In₂O₃:H layer was directly deposited on top, also at 100 °C. Figure 3.11 shows the measured carrier lifetime for the different process steps. As can be seen, an \( V_{oc} \) of 710 mV was achieved after the crystallization of the In₂O₃:H layer at 200 °C. This is just slightly lower than the 718 mV which was obtained for the similar stack using the home-built ALDii reactor for the MoOₓ deposition (see Section 3.3.2) and indicates a good level of passivation can be achieved using the ALD process on the OpAL reactor, even though RBS measurements showed a high level of impurities in the films.

![Figure 3.11](image-url)  
Figure 3.11. Injection-dependent minority carrier lifetime for a stack of a-Si:H/MoOₓ/In₂O₃:H, after each processing step. The (orange) squares indicate the implied Voc under 1 sun illumination. The a-Si:H and MoOₓ thicknesses were 5 nm.
After it was confirmed that good passivation can be achieved with the MoO\textsubscript{x} process on the OpAL reactor, two initial tests of the MoO\textsubscript{x} layer in actual solar cells were done in collaboration with Energieonderzoek Centrum Nederland (ECN). For these tests, ECN provided solar cells with a standard back side consisting of a-Si:H(i)/a-Si:H(n)/TCO/Ag-contact, while the front side was deposited at TU/e. The front side of Cell A consisted of 5 nm intrinsic a-Si:H, 5 nm MoO\textsubscript{x} and around 75 nm In\textsubscript{2}O\textsubscript{3}:H, while Cell B was deposited with an additional ultrathin Al\textsubscript{2}O\textsubscript{3} layer between the a-Si:H(i) and MoO\textsubscript{x} layers. This Al\textsubscript{2}O\textsubscript{3} layer served as a protection layer for the a-Si:H and can induce additional band bending (see Section 3.3.1). To prevent a barrier in the cell only 4 ALD cycles were performed for the deposition, which corresponds to a layer of roughly 0.5 nm thick.

To characterize the solar cells, Suns-V\textsubscript{oc} measurements were performed.\textsuperscript{119,120} In contrast to the measurement of the \textit{i}V\textsubscript{oc}, this method measures the actual, external V\textsubscript{oc}. The method does not, however, require a full solar cell. As long as the solar cell contains the selective layers on the front and back side the V\textsubscript{oc} can be measured. This is done by placing a contact on the front and back side of the cell and illuminate the cell with a short light flash. The incoming light flash generates electron-hole pairs, which induces a voltage difference over the cell. Since no current is drawn from the cell, the measured voltage corresponds to open-circuit voltage. The results of this measurement on the two different cells are shown in Figure 3.12(a). As can be seen, an very low V\textsubscript{oc} of 289 mV is measured under 1 sun illumination for Cell A. Due to the additional ultrathin Al\textsubscript{2}O\textsubscript{3} layer Cell B performs slightly better, reaching a V\textsubscript{oc} of 429 mV, but compared to the expected V\textsubscript{oc} in the 700 mV range this is still very low. The bad performance of the cells is expected to be caused by either an insufficient level of hole selectivity, or by a parasitic current along the edge of the cell, which prevents the build up of a voltage difference across the cell. As explained in Section 3.A, a comparison of the implied V\textsubscript{oc}, measured by lifetime measurements, and the external V\textsubscript{oc} from the Suns-V\textsubscript{oc} measurement can give information about the hole selectivity. Unfortunately it was not possible to measure the \textit{i}V\textsubscript{oc} on Cells A and B, since a metallic electrode was already deposited on the backside, which impedes the measurement of the induced photoconductance.

To further study the performance of the cells, the pseudo efficiency of the cells was calculated. By measuring the incoming photocurrent on a reference cell as a function of the measured voltage, the so-called pseudo current is determined, which can be used to create a pseudo IV-curve, as is shown in Figure 3.12(b). For this pseudo IV-curve the \textit{J}\textsubscript{sc} from the optical simulations is used as short-circuit current (see Section 3.B). Using Equation 3.1 and the measured values for the V\textsubscript{oc} and \textit{FF} the pseudo efficiency is calculated. Note that the fill factor \textit{FF} is given by \(P_{\text{max}}/(\textit{J}_{\text{sc}} \times \textit{V}_{\text{oc}})\), and is mainly influenced by resistive effects in the solar cell.\textsuperscript{121}
3.D. Initial results on OpAL™ reactor

As can be seen in Figure 3.12(b), low efficiencies of 8.7 % and 13.9 % are found for Cells A and B, respectively, which is caused by the very low $V_{oc}$. The cells do however show a reasonable $FF$, which shows that cells potentially have a high efficiency, but are limited by the $V_{oc}$. It should be noted that the solar cells were only made as a preliminary test, and the MoO$_x$ deposition on the OpAL reactor is still to be optimized before additional solar cells are prepared. An outlook to further research and possible solutions in order to improve the performance of the cells will be given in Chapter 4.

Figure 3.12. (a) Suns-$V_{oc}$ measurements on two cells with MoO$_x$ hole selective layers. (b) Pseudo IV-curve for the two solar cells. The a-Si:H and MoO$_x$ thicknesses were 5 nm and 4 ALD cycles were performed for the Al$_2$O$_3$ deposition.
Process development & material properties

A novel ALD process for the deposition of MoO$_x$ using (N$^\prime$Bu)$_2$(NMe$_2$)$_2$Mo and O$_2$ plasma was successfully developed on the home-built ALDii reactor. The use of an O$_2$ plasma as reactant enabled the deposition of high-purity films at low temperatures, which is a requirement for the application in SHJ solar cells. Self-limiting ALD behavior was confirmed and an optimized ALD recipe with a precursor dosing time of 6 s and plasma exposure time of 4 s was obtained. For deposition temperatures between 50 °C and 250°C a GPC between 0.72 Å and 0.93 Å was found, while the GPC increased up to 1.88 Å for higher temperatures due to a transition to polycrystalline growth occurring during film deposition.

The material properties were extensively characterized as a function of deposition temperature. XRD measurements confirmed amorphous films up to a deposition temperature of 250°C, while films deposited at higher temperatures were found to be crystalline. The material was of high purity for all deposition temperatures, with C and N contamination below the RBS detection limit of 3 at. % and 2 at. %, respectively. Moreover, a H content between 3 at. % and 11 at. % was found using ERD. The optical Tauc band gap was determined to vary between 2.77 eV and 2.87 eV for amorphous films and was 2.92 eV for polycrystalline films.

Potential for SHJ solar cells

The potential of the newly developed ALD process for the deposition of thin MoO$_x$ layers for application in SHJ solar cells was demonstrated. Lifetime measurements showed an excellent implied $V_{oc}$ of 710 mV for a stack of a-Si:H/MoO$_x$/In$_2$O$_3$:H with an a-Si:H layer of 3 nm thick. Moreover, inserting an additional ultrathin ($\sim$1 nm) layer of Al$_2$O$_3$ further increased the $iV_{oc}$ to 718 mV. Optical simulations showed an estimated gain in $J_{sc}$ of 1 mA/cm$^2$ for a solar cell using 5 nm MoO$_x$ as hole selective layer, in comparison to a conventional solar cell with 10 nm p-type a-Si:H.
Chapter 4. Conclusion and outlook

Transfer to OpAL™ reactor

As was shown in Section 2.E the MoO\textsubscript{x} ALD process was also developed on the OpAL™ reactor, so that In\textsubscript{2}O\textsubscript{3}:H can be deposited directly on top of the MoO\textsubscript{x} layer without breaking the vacuum. Self-limiting growth was confirmed for a deposition temperature of 100 °C and a transition from amorphous to polycrystalline transition was found for higher temperatures, in line with the results from the home-built reactor. However, a very high GPC of 1.21 Å was found at a deposition temperature of 100 °C, compared to 0.72 Å on the home-built reactor. Considering the saturating nature of ALD, this large difference is not expected for ideal ALD, but is thought to be caused by the incorporation of impurities. RBS measurements showed a high level of impurities in the films, which should be resolved before additional solar cells are made. Two measures that can possibly reduce the impurity content are lowering the precursor residence time and increasing the ion energy, which are both achieved by lowering the working pressure. At high deposition temperatures an extremely high GPC up to 2.7 Å was found, which ask for further development of the process at high deposition temperatures. Most importantly, self-limiting behavior should be confirmed at high temperatures.

Hole selectivity & contact resistance

Although the potential of ALD MoO\textsubscript{x} films for SHJ solar cells in terms of passivation and optical properties was shown for several types of stacks in Chapter 3, two important things are still to be investigated.

Firstly, the hole selectivity of the ALD MoO\textsubscript{x} films should be confirmed. Equilibrium band calculations for the solar cell with MoO\textsubscript{x} showed an upward band bending similar to a conventional SHJ with a-Si:H(p), but experiments are needed to verify this, especially since the height of the band bending depends on the work function of the MoO\textsubscript{x}. Therefore, the MoO\textsubscript{x} work function should be measured either using a Kelvin probe or by XPS. Preliminary measurements of the work function by XPS yielded values between 4.3 eV and 5.2 eV, depending on the measurement setting and the surface treatment. It was however shown that the measurement is affected by the XPS exposure and higher values around 5.5 eV for a contaminated surface and 6.6 eV for a UV-O\textsubscript{3} treated are expected. Therefore, an XPS setup that enables the use of low intensity X-rays and variation of the distance between the X-ray source and sample should be used in order to obtain a correct value for the work function. In addition, the band bending in the a-Si:H/MoO\textsubscript{x}/In\textsubscript{2}O\textsubscript{3}:H stacks should be measured by surface photovoltage spectroscopy (SPV). These measurements are currently under preparation in collaboration with the Fraunhofer Institute for Solar Energy Systems. Another way to confirm the hole selectivity is to compare the Sinton lifetime measurements with Suns-V\textsubscript{oc} measurements, as was explained in Section 3.D.\textsuperscript{115}

Secondly, contact resistance measurements should be performed to verify if a sufficient tunneling current can be achieved with an Al\textsubscript{2}O\textsubscript{3} layer of ~1 nm. Although the stacks with Al\textsubscript{2}O\textsubscript{3} passivation layers as discussed in Section 3.3.2 showed very good results in terms of iV\textsubscript{oc}, it should be kept in mind that the Al\textsubscript{2}O\textsubscript{3} layer can lead to a barrier in the cells. However, based on previous studies it is expected that a layer of just ~1 nm thick will still be workable. If this is confirmed by the contact resistance measurements, the use of an Al\textsubscript{2}O\textsubscript{3} passivation layer could be another route to further increasing the efficiency of the SHJ solar cell.
Application in solar cells

Two first initial test cells were made in collaboration with Energieonderzoek Centrum Nederland (ECN), but showed poor results, indicating the MoO$_x$ films should be further optimized and several checks should be done before more cells are made. After the remaining issues have been investigated and, if necessary, resolved, a new batch of solar cells with an ALD MoO$_x$ hole selective layer should be made to confirm the predicted gain in $J_{sc}$ and to verify if the low conductivity of MoO$_x$ does not cause a barrier in the cell. Collaborations are currently going on with ECN and the Fraunhofer Institute for Solar Energy Systems to test the MoO$_x$ ALD process in solar cell devices.

Alternative routes to a more efficient SHJ solar cell

An alternative route to minimize the parasitic absorption in the front side of the SHJ solar cell would be to use other high work function metal oxides, such as NiO$_x$, VO$_x$ and WO$_x$, as hole selective layers. Just like MoO$_x$, these materials have shown their potential as hole selective layers in OPV. Moreover, the a-Si:H(i) passivation layer is still responsible for substantial absorption, which could be reduced by using a more transparent material for passivation, for instance Al$_2$O$_3$ or SiO$_x$. More transparent TCOs are another approach to reduce absorption losses on the front side, although the recently developed ALD In$_2$O$_3$:H and sputtered Zn-doped In$_2$O$_3$ already show an excellent transparency which is close to the fundamental limit. Moreover, the IBC (interdigitated back contact) SHJ design shows great potential in achieving higher efficiencies, although the complex design makes it less ideal for large scale production.

Other applications and spin-offs

In addition to SHJ solar cells, the newly developed ALD process might be suited for application in other types of solar cells, for instance in perovskites and organic PV, where MoO$_x$ has already been used as hole extractor. Note that the novel ALD process yields good material properties at a deposition temperature as low as 50 °C, which fits nicely with the requirement for low processing temperatures of these types of solar cells.

Moreover, a project has already started where the MoO$_x$ ALD films are used for the synthesis of MoS$_2$ by plasma sulphurization. Ultrathin, 2D layers of MoS$_2$ have received great interest, since they are said to be a better alternative to graphene. In addition, the novel ALD process is used in another project to deposit a catalytic Co-Mo substrate by interchanging ALD cycles of MoO$_x$ and CoO$_x$, which, according to literature, can be used to grow single wall carbon nanotubes. As mentioned in the introduction, MoO$_x$ is being used for many other applications, such as batteries, gas sensors and optoelectronic devices, and the novel ALD process presented in this report might lead to improvement of these devices or maybe even new applications, especially since ALD enables the deposition of conformal films on nanostructures.
Acknowledgments

Of course I could not have done this graduation project all by myself and there are many people I wish to acknowledge for their support during the last year. First of all the technicians for their assistance with experiments and keeping all the systems running. Casper and Cristian in particular: Casper, your help with the ALDii reactor when it was just finished has been essential, and Cristian, thank you for the assistance with the OpAL experiments and other cleanroom-related things.

Bart, thank you for your supervision, I think you deserve a 7.5! No, but seriously, thank you for your outstanding guidance and advice. When I started this project I did not know much about solar cells, and in you I found a great teacher. Moreover, your help with all the new analysis techniques was invaluable and I really appreciate you were always available for help and comments on new results. Erwin, I also want to thank you for your supervision. I think you are setting a great standard for the work we do within PMP; you’re positive criticism always motivates us to do the best we can. Thank you for taking the time during your holidays to read and comment on this thesis! (Or in other words, sorry I provided you with work during your holidays.) Also, I’m very happy you gave me the chance to present this work at the AVS symposium in San Jose next October.

My recognition also goes out to the other master students from the PMP group. Especially Maarten, Joris and Lidewij: Thank you for all the awesome times, the awesome lunches and the always funny coffee/tea breaks. I think we should still do that weekend in Porto or Warsaw, or whatever! In addition I would like to acknowledge several other people from the PMP group: Nick, for giving me the chance to develop the MoO₃ ALD process and for the helpful discussions we had; Akhil for involving me in the MoS₂ project, it was good to see the MoO₃ process found a second application within such a short time; Harm for many fruitful discussions and providing comments on the process paper; Jan-Willem for sharing your SE expertise with me; and of course all the other people in the PMP group, I think we make up a cool team!

Finally I would like to thank my parents and brother enormously, since they made it possible for me to study, provided me with a home and greatly supported me during my studies and the last year especially.

I would like to end this thesis by saying that I have greatly enjoyed the last year working on this project. The available resources are great and the level of expertise within the group is outstanding, but what is maybe more important is the open and friendly the atmosphere. I’m extremely looking forward to four more years in the Plasma & Materials Group.
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Bibliography


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Bibliography


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Appendix A

Matlab script for work function calculation

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% XPS work function determination 
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% This Matlab script calculates the WF of a certain material by using Au as% a reference. Manuals on how to obtain the XPS data for this calculation % can be found in: 'Calibration of Photoemmission Spectra and Work Function% Determination' by Dr. Rudy Schlaf and in the manual of the XPS setup. %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% NOTE: Matlab takes quite a while (~30s) to read in the data from the % .xls files. So please be patient if it takes a while:) %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% OUTPUT: Program saves a couple of files: %
% 1: Shifted spectrum data (both cut-off & Fermi) to .xls file. %
% 2: Calculated Cut-off & WF values (for each etch level)to .xls %
% 3: Picture of Cut-off & Fermi level for all etch levels combined to .png %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% DATA FILE REQUIREMENTS: %
% First export the data in Avantage to two .xls or .xlsx files with the % standard reporting settings. One file for the Au ref. and one file for % the sample of interest (SOI). If multiple etch levels are used for the % SOI the data should be stacked in the Avantage software %
% ('Display Modes\Display selected data in 2D chart mode') and then % exported to one .xls(x) file for that sample. Leave the cut-off energies% in Kin.E. and the Fermi in B.E. This Matlab function will then read in % the correct columns of the raw data files and convert the K.E. to B.E. %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% CALCULATION PROCEDURE: %
% 1: Read data from .xlsx files and select the right columns. %
% 2: Convert cut-off spectra of Au and SOI from Kinetic to Binding energy %
% 3: Shift the Fermi level of the Au reference spectrum to 0 B.E.. %
% This is done by calculating the inflection point at the valence band %
% \( \frac{d}{dx}=\text{max, } \frac{d^2}{dx^2}=0 \). %
% 4: Determine cut-off value of Au spectrum by fitting a linear function. %
% 5: Calculate WF of Au: Using the cut-off value (COV) the WF of the Au %
% ref. sample is calculated (WF = \( h\nu - \text{COV}_{\text{AU}} \)) and checked (should be %
The energy $h\nu$ of the Al K-alpha photons is 1486.6eV. 

6: Shift spectrum of SOI with the same value as the Au ref. 

This can be done since the Fermi levels of both samples are the same (the samples are electrically connected on the stage).

7: Determine cut-off value for SOI, again by fitting a linear function through the linear region at the cut-off.

8: Calculate WF for SOI: $WF = h\nu - COV_{SOI}$

% Read data

1. Select data files

```matlab
[FileAu,PathAu]=uigetfile({'*.xlsx;*.xls','XPS Data Files (*.xls,*xlsx)'},...
    'Select the data file for the Gold reference');

[FileSOI,PathSOI]=uigetfile({'*.xlsx;*.xls','XPS Data Files (*.xls,*xlsx)'},...
    'Select the data file for the sample of interest');

sample_name=strsplit(FileSOI,'.'); sample_name=char(sample_name(1));
FileAu_name=strsplit(FileAu,'.'); FileAu_name=char(FileAu_name(1));

sdir=[PathSOI,sample_name,'_WF']; %Directory where images and data will saved.
ex=exist(sdir,'dir');
if ex==0; mkdir(sdir); %Make directory if it doesn't exist.
end

if exist([PathAu FileAu_name '_WF_calc.xls'],'file');
    Au_calc=1;
else Au_calc=0;
end

if Au_calc==1;
    [Au_RES]= xlsread([PathAu 'Gold_WF_calc.xls']);
    IFP=Au_RES(1); % COV_Au=Au_RES(2);
    % WF_Au=Au_RES(3);
else Au_calc=0;
end
tic
[~,sheets_Au]=xlsinfo([PathAu,FileAu]);
if any(strcmp(sheets_Au,'cut-off')); c_Au=1;
    Au_cutoff_raw=xlsread([PathAu,FileAu],'cut-off');
elseif any(strcmp(sheets_Au,'Cut-off')); c_Au=1;
    Au_cutoff_raw=xlsread([PathAu,FileAu],'Cut-off');
else c_Au=0;
    display(' ERROR');
    display(' Worksheet with cut-off data for Au is not found'...
        'or does not exist.')
    display(' Please check if the naming is correct.');
    display('');
    return
end
if any(strcmp(sheets_Au,'Fermi')); f_Au=1;
    Au_fermi_raw=xlsread([PathAu,FileAu],'Fermi');
elseif any(strcmp(sheets_Au,'fermi')); f_Au=1;
```
Appendix A. Matlab script for work function calculation

```matlab
Au_fermi_raw = xlsread([PathAu, FileAu], 'fermi');
else
    f_Au = 0;
    display(' ERROR');
    display(' Worksheet with Fermi data for Au is not found'...
    'or does not exist. Please check the naming.');
    display(' Program cannot calculate WF and will stop. ');
    display(' ');
end

% Logical array to cut out the correct range of raw cut-off data file:
tmp1 = ~isnan(Au_cutoff_raw(:,1));
% Logical array to cut out the correct range of raw Fermi data file:
tmp2 = ~isnan(Au_fermi_raw(:,1));

% Cut out Kin.E. & Intensity
Au_cutoff = [Au_cutoff_raw(tmp1,1), Au_cutoff_raw(tmp1,3)];
% Convert from Kin.E. to BE.
Au_cutoff(:,1) = 1486.6 - Au_cutoff(:,1);
% Cut out B.E. & Intensity
Au_fermi = [Au_fermi_raw(tmp2,1), Au_fermi_raw(tmp2,3)];
end

%% Read SOI Data
[~, sheets_SOI] = xlsfinfo([PathSOI, FileSOI]);
if any(strcmp(sheets_SOI, 'cut-off'))
    c_SOI = 1;
    SOI_cutoff_raw = xlsread([PathSOI, FileSOI], 'cut-off');
elseif any(strcmp(sheets_SOI, 'Cut-off'))
    c_SOI = 1;
    SOI_cutoff_raw = xlsread([PathSOI, FileSOI], 'Cut-off');
else
    c_SOI = 0;
    display(' ERROR');
    display(' Worksheet with cut-off data for SOI is not found' ... 
    'or does not exist.');
    display(' Please check if the naming is correct.');
    display(' ');
    return
end

if any(strcmp(sheets_SOI, 'Fermi'))
    f_SOI = 1;
    SOI_fermi_raw = xlsread([PathSOI, FileSOI], 'Fermi');
elseif any(strcmp(sheets_SOI, 'fermi'))
    f_SOI = 1;
    SOI_fermi_raw = xlsread([PathSOI, FileSOI], 'fermi');
else
    f_SOI = 0;
    display(' WARNING');
    display(' Worksheet with Fermi data for SOI does not exist.');
    display(' Program will continue to calculate WF of SOI,'...
    'but will not plot Fermi level.');
    display(' ');
end

% Determine the number of etch levels (i.e. determine the number of columns 
% with intensity data) And determine which range of data file needs to be used: 

% Cut-off:
% Logical array which is 0 if entry is nan, to cut out the cut-off data
tmp_co = ~isnan(SOI_cutoff_raw(:,1));
```

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iB_co=find(tmp_co); % Indices of not nan entries.
w_co=find(~isnan(SOI_cutoff_raw(iB_co(1),:))); % Indices of 1st row of needed data
etch_levels=w_co(end)-w_co(2)+1; % Number of etch levels
% Cut out Kin.E. & Intensity:
% first column contains K.E., others contain intensity data for each etch level)
SOI_cutoff=[SOI_cutoff_raw(tmp_co,1),SOI_cutoff_raw(tmp_co,w_co(2):w_co(end))];
SOI_cutoff(:,1)=1486.6-SOI_cutoff(:,1); % Convert from Kin.E. to BE.

% Fermi:
if f_SOI==1;
% Logical array which is 0 if entry is nan, to cut out the range of raw fermi data
tmp_f=~isnan(SOI_fermi_raw(:,1));
iB_f=find(tmp_f);
w_f=find(~isnan(SOI_fermi_raw(iB_f(1),:)));
tmp_f=~isnan(SOI_fermi_raw(:,1));
SOI_fermi=[SOI_fermi_raw(tmp_f,1),SOI_fermi_raw(tmp_f,w_f(2):w_f(end))];
% Cut out B.E. & Intensity
end

%% Plot unshifted Au data
if Au_calc==0;
    fmin=ceil(min(Au_fermi(:,1))); fmax=floor(max(Au_fermi(:,1)));
cmin=ceil(min(Au_cutoff(:,1))); cmax=floor(max(Au_cutoff(:,1)));
figure(1); clf(1); set(1,'Units','Centimeters','Position',[22,2,22,23.5]);
figure(1); set(1,'name',['Au reference: Cut-off & Fermi level. (' FileAu ')]);
subplot(221)
plot(Au_cutoff(:,1),Au_cutoff(:,2));
xlabel('Binding energy (eV)'); title('Au Cut-off, unshifted');
xlim([cmin,cmax]); set(gca,'xdir','reverse'); set(gca,'YTickLabel',');

subplot(222)
plot(Au_fermi(:,1),Au_fermi(:,2));
xlabel('Binding energy (eV)');
xlim([fmin,fmax]); set(gca,'xdir','reverse'); title('Au Fermi, unshifted');
set(gca,'YTickLabel',');
end

%% Plot unshifted SOI data
cmin=ceil(min(SOI_cutoff(:,1)));
cmax=floor(max(SOI_cutoff(:,1)));
figure(3); clf(3); set(3,'Units','Centimeters','Position',[22,2,22,23.5]);
figure(3); set(3,'name',['SOI: Cut-off & Fermi level. (' sample_name ')]);
subplot(221)
plot(SOI_cutoff(:,1),SOI_cutoff(:,2:end));
xlabel('Binding energy (eV)'); title('SOI Cut-off, unshifted');
xlim([cmin,cmax]); set(gca,'xdir','reverse'); set(gca,'YTickLabel',');
if f_SOI==1;
    fmin=ceil(min(SOI_fermi(:,1)));
    fmax=floor(max(SOI_fermi(:,1)));
    subplot(222)
    plot(SOI_fermi(:,1),SOI_fermi(:,2:end));
xlabel('Binding energy (eV)');
end
Appendix A. Matlab script for work function calculation

```matlab
xlim([fmin,fmax]); set(gca,'xdir','reverse'); title('SOI Fermi, unshifted');
set(gca,'YTickLabel', '');
end

%% Determine inflection point (IFP) to shift Ef to 0 eV
if Au_calc==0;
  dBE=Au_fermi(2,1)-Au_fermi(1,1);
div1=zeros(length(Au_fermi)-2,1);
for k=2:length(Au_fermi)-1;
  div1(k-1)=(Au_fermi(k+1,2)-Au_fermi(k-1,2))/(2*dBE);
end
div2=zeros(length(div1)-2,1);
for k=2:length(div1)-1;
  div2(k-1)=(div1(k+1)-div1(k-1))/(2*dBE);
end

% Select range to search for maximum in 1st derivative
[~,ib]=min(abs(Au_fermi(:,1)--29.5));
[~,ie]=min(abs(Au_fermi(:,1)--30.5));

iIFP=find(div1==max(div1(ib:ie)))+1;
IFP=Au_fermi(iIFP,1); %Inflection point
figure(2); clf(2); set(2,'name','Calculation of inflection point');
set(2,'Units','Centimeters','Position',[22,2,22,10]);
subplot(121)
plot(Au_fermi(2:end-1,1),div1)
xlim([-32,-27]); set(gca,'xdir','reverse'); xlabel('Binding energy (eV)');
text(IFP-0.06,div1(iIFP-1)*1.2,num2str(IFP)); ylabel('dI/dE');
line([IFP,IFP],get(gca,'Ylim'),'color','r');
subplot(122)
plot(Au_fermi(3:end-2,1),div2,[0,0]);
xlim([-32,-27]); set(gca,'xdir','reverse'); xlabel('Binding energy (eV)');
line([IFP,IFP],get(gca,'Ylim'),'color','r');
figure(1); subplot(223); hold on; yl=get(gca,'Ylim');
line([IFP,IFP],[0,yl(2)*0.35],'linestyle','--');
text(IFP+0.3,yl(2)*0.35,num2str(IFP));
end

%% Shift spectra so E_Fermi = 0 eV & Plot

% AU:
if Au_calc==0;
  Au_cutoff_s=[Au_cutoff(:,1)-IFP,Au_cutoff(:,2)]; % Au cut-off shifted
  Au_fermi_s=[Au_fermi(:,1)-IFP,Au_fermi(:,1)]; % Au fermi shifted
  fmin_au=ceil(min(Au_fermi_s(:,1)));
fmax_au=floor(max(Au_fermi_s(:,1)));
cmin_au=ceil(min(Au_cutoff_s(:,1)));
cmax_au=floor(max(Au_cutoff_s(:,1)));
figure(1)
subplot(223)
plot(Au_cutoff_s(:,1),Au_cutoff(:,2));
xlim([cmin_au,cmax_au]); set(gca,'xdir','reverse');
```
xlabel('Binding energy (eV)'); title('Au Cut-off, shifted');
set(gca,'YTickLabel','
 subplot(224)
plot(Au_fermi(:,1),Au_fermi(:,2));
xlabel('Binding energy (eV)');
set(gca,'xdir','reverse'); title('Au Fermi, shifted');
xlim([fmin_au,fmax_au]); set(gca,'YTickLabel','
 end

% SOI:
% Cut-off
SOI_cutoff_s=[SOI_cutoff(:,1)-IFP,SOI_cutoff(:,2:end)];% SOI cut-off shifted
cmin=ceil(min(SOI_cutoff_s(:,1)));
cmax=floor(max(SOI_cutoff_s(:,1)));
figure(3)
 subplot(223)
plot(SOI_cutoff_s(:,1),SOI_cutoff_s(:,2:end));
xlim([cmin,cmax]); set(gca,'xdir','reverse');
xlabel('Binding energy (eV)'); title('SOI Cut-off, shifted');
set(gca,'YTickLabel','
 end
% Fermi
if f_SOI==1;
SOI_fermi_s=[SOI_fermi(:,1)-IFP,SOI_fermi(:,2:end)]; % SOI fermi shifted
fmin=ceil(min(SOI_fermi_s(:,1)));
fmax=floor(max(SOI_fermi_s(:,1)));
 subplot(224)
plot(SOI_fermi_s(:,1),SOI_fermi_s(:,2:end));
xlabel('Binding energy (eV)'); title('SOI Fermi, shifted');
xlim([fmin,fmax]); set(gca,'YTickLabel','
 end

%% Save shifted spectra of SOI to .xlsx file
if f_SOI==1;
dl=length(SOI_fermi_s)-length(SOI_cutoff_s); ad=zeros(dl,etch_levels+1);
spectra=[[SOI_cutoff_s;ad],SOI_fermi_s]; spectra=[['Cut-off B.E. (eV)',num2cell(0:etch_levels-1),'Fermi B.E. (eV)',...
    num2cell(0:etch_levels-1)];num2cell(spectra)];
elseif f_SOI==0
spectra=SOI_cutoff_s; spectra=[['Cut-off B.E. (eV)',num2cell(0:etch_levels-1)];num2cell(spectra)];
end

xlswrite([sdir,sample_name,'_WF_spectra.xlsx'],spectra);

%% Calculate cut-off value

% Au:
if Au_calc==0;
% 1: Select linear part at cut-off region
dy=diff(Au_cutoff_s(:,2)); % Calculate intensity increase at each point (=dy).
Appendix A. Matlab script for work function calculation

```matlab
[dy_max,imax]=max(dy); % Find max dy near cut-off, imax=index of max. dy
c=1;
for k=imax-3:1:imax+3; % Scan points nearby point with max dy.
    if dy(k)>dy_max*0.6; % Allow point to linear region if dy within 40% of max dy.
        lin(c)=k;
        c=c+1;
    end
end
%
% 2: Fit first order polynomial through linear part
p=polyfit(Au_cutoff(:,1),Au_cutoff(:,2),1); % Linear fit at cut-off
figure(1); subplot(223); hold on;
plot(Au_cutoff(:,1),Au_cutoff(:,2),'r'); % Plot points in lin. region
COV_Au=-p(2)/p(1); % Cut-off value Au
fAU = @(x) p(1)*x+p(2); % Fitted curve at cut-off
xm=(max(Au_cutoff(:,2))-p(2))/p(1);
plot([COV_Au,xm],[fAU(COV_Au),fAU(xm)],'k'); % Plot linear part
str=sprintf('Cut - off = %0.2f eV',COV_Au);

% 3: Calculate WF & write text to figure
WF_Au=1486.6-COV_Au; % Work function Au (~5.1eV)
wstr=sprintf(' WF = \n1486.60 - %0.2f =\n%0.2f eV',COV_Au,WF_Au);
yl=get(gca,'ylim'); yl=yl(2);
str='%0.2f eV','WF_Au');
text(COV_Au-0.2,yl*0.05,str,'Fontsize',11,'Edgecolor','k');
end
%
% SOI (for each etch level separately)
WF=zeros(etch_levels,1); COV=zeros(etch_levels,1);
RES=zeros(etch_levels,3);
figure(4); clf(4); set(4,'Units','Centimeters','Position',[22,2,22,10]);
for etch_level=0:etch_levels-1;
    t=etch_level+2;
    % 1: Plot (shifted) spectra (only current etch level)
    figure(4); clf(4); set(4,'name',['Etch level ' num2str(etch_level)]);
    subplot(121);
pplot(SOI_cutoff(:,1),SOI_cutoff(:,t));
xlim([cmin,cmax]); set(gca,'xdir','reverse');
xlabel('Binding energy (eV)'); title('SOI Cut-off, shifted');
set(gca,'YTickLabel','');
if f_SOI==1
    subplot(122)
pplot(SOI_fermi(:,1),SOI_fermi(:,t));
xlabel('Binding energy (eV)');
set(gca,'xdir','reverse'); title('SOI Fermi, shifted');
xlim([fmin,fmax]); set(gca,'YTickLabel','');
end
% 2: Select linear part at cut-off region
tic
dy=diff(SOI_cutoff(:,t));
[dy_max,imax]=max(dy); % max slope at cut-off, imax=index of max. dy
% Other 'dys' are allowed to the linear region if they are withing 40% of
% the maximum dy
c=1;
```

lin=[];
for k=imax-3:1:imax+3;
  if dy(k)>dy_max*0.6;
    lin(c)=k;
    c=c+1;
  end
end

% 3: Fit first order polynomial through linear part
p=polyfit(SOI_cutoff_s(lin,1),SOI_cutoff_s(lin,t),1);
figure(4); subplot(121); hold on;
plot(SOI_cutoff_s(lin,1),SOI_cutoff_s(lin,t),'r');
COV_SOI=-p(2)/p(1); % Cut-off value SOI
WF_SOI=1486.6-COV_SOI; % Work function SOI (Should be ~5.1eV)
fSOI = @(x) p(1)*x+p(2); % Linear fit at cut-off
xm=(max(SOI_cutoff_s(:,t))-p(2))/p(1);
plot([COV_SOI,xm],[fSOI(COV_SOI),fSOI(xm)],'k');
cstr=sprintf('Cut off = %0.2f eV',COV_SOI);
wstr=sprintf('WF = %0.2f eV',WF_SOI);
yl=get(gca,'ylim'); yl=yl(2);
text(COV_SOI-0.2,yl*0.05,cstr);
text(cmax-0.25,yl*0.65,wstr,'Fontsize',11,'Edgecolor','k');
text(cmax-0.25,yl*0.85,[['Etch level ',num2str(etch_level)],[['Fontsize',11,'Edgecolor','k']]);

% Save figure & WF
saveas(4,[sdir,'Cut-off_Fermi_',sample_name,'EtchLevel_',num2str(etch_level),'.png']);
WF(etch_level+1)=WF_SOI;
COV(etch_level+1)=COV_SOI;
RES(etch_level+1,:)= [etch_level;COV_SOI;WF_SOI];

end
%% Plot WF vs etch level and save image
if etch_levels>1;
  figure(5); set(5,'name',['WF vs etch level. (' sample_name ')']);
  plot(0:1:etch_levels-1,WF,'o-');
  xlabel('Etch level'); set(gca,'xtick',0:1:etch_levels-1);
  ylabel('Work function (eV)');
  saveas(5,[sdir,'WF vs Etch Level.png']);
end
%% Save shifted spectra and calculated WF
RES=[['Etch level','Cut-off value (eV)','Work Function (eV)'];num2cell(RES)];
xlswrite([sdir,sample_name,'_WF_calc.xls'],RES);
if Au_calc==0;
  RES_Au=([IFP,COV_Au,WF_Au];
  RES_Au=[['Inflection point','Cut-off value (eV)',...
  'Work Function (eV)'];num2cell(RES_Au)];
xlswrite([Path_Au,File_Au '_WF_calc.xls'],RES_Au);
end