Crystalline silicon Heterojunction solar cells

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ABSTRACT

This work is a slight research on silicon heterojunction solar cells which have been of great interest recently. The aim is to span fabrication, characterization and simulation and to reach a broad but shallow knowledge about this devices. Within heterojunction solar cells, this work is particularly focused on amorphous silicon/crystalline silicon (a-Si/c-Si) heterojunction solar cells and Transition-Metal-Oxide (TMO) silicon heterojunction solar cells (TMO/c-Si).

TMO started being of interest very recently because they can substitute a-Si in a solar cell lowering fabrication costs while achieving relatively good performance. Unlikely, it is not clear why it can play the same role as a-Si since they are very different materials. Therefore simulating TMO based devices is still far from being reliable. Simulations of a-Si heterojunction solar cells have been performed since it seems to be the starting point of the road to simulating TMO.

The fabrication and characterization processes are almost the same for the two types of solar cell. Since the final aim is to understand TMO heterojunction solar cells, this part is dedicated to them. Three different TMOs heterojunction solar cells have been fabricated and characterized which are $\text{MoO}_x$, $\text{WO}_x$ and $\text{V}_2\text{O}_5$ while the simulation has focused on a-Si. The work has been carried out collaborating with a research group from electronics department of the UPC (Universitat Politèctica de Catalunya). Silvaco ATLAS electronic device simulator has been used to reproduce the a-Si HIT (Heterojunction with Intrinsic Thin layer) solar cell figures of merit.
Chapter 1

Introduction

1.1 Basics of solar cells

1.1.1 Principles of operation

Solar cells are electronic devices which absorb light to generate electricity. This conversion is possible due to the semiconductor materials since they have a low bandgap energy that enables electronic transitions from valence band to conduction band energy levels. This transitions can be produced by the absorption of an external photon. Specifically, when a photon is absorbed by a valence band electron, it jumps to the conduction band becoming able to flow through the material. Consequently, an electron vacancy is generated in the valence band, this vacancy is called hole and it can be occupied by a neighbor valence electron creating a new vacancy so that there is a hole displacement. In other words a photon generates a pair of charge carriers able to diffuse through the material until they reach other material (so they can be collected by the contacts to generate electrical current) or they recombine(electron returns to the valence band occupying a hole so there is no current generation).

The aim is to collect as much carriers as possible, for this reason solar cells usually have a p-n structure. This means that there are two zones, one doped with acceptor impurities so that it exhibits a higher holes concentration (p-zone), another doped with donor impurities that provides a higher electron concentration (n-zone). Then the structure of a simple solar cell could be one similar to the one shown in Figure 1.1. Due to the difference of carrier concentrations between the two zones there is a diffusion which creates an electric field that is represented with an energy band curvature. This electric direct the electrons to the n-zone (to the right hand side of the picture) and the hole to the p-zone (to the left hand side of the picture). In this case, when the solar cell is illuminated, the useful carrier pair generation take place in the p zone, thus excited electrons can easily pass through the n-zone and be collected in the front contact while holes cannot pass through the n-zone thus they can be collected in the rear contact generating electrical current.
1.1.2 Parts of a solar cell

As we will briefly comment in Section 1.3 there are many types of solar cells. However, all of them exhibit the same basic structure which contains the absorption layer, semipermeable layers\(^1\), a transparent front contact, and the metallic front and rear contacts.

The **absorption layer** is where the most part of the photons are absorbed and usually is the thicker layer.

**Semipermeable layers** are parts of the cell that basically advantage the flow of one type of charge carriers and blocks the other. Therefore there are electron transport layers and hole transport layers. For example, sometimes is used a p-i-n junction (shown at Figure 1.2). In this case, the carriers are mostly generated in the intrinsic zone, p-zone blocks the excited electrons coming from i-zone enabling holes to pass through, n-zone does the opposite blocking holes and enabling electrons to pass through. So this layers achieve better hole and electron collection, thus, they improve the solar cell efficiency.

**Transparent front contact.** Notice that Figure 1.2 also present an extra layer labeled as Transparent Conducting Oxide (TCO). This layer is a highly doped oxide which basically acts as a transparent front contact. In Section 3.2.5 indium tin oxide (ITO), which is a particular TCO, is described in more detail.

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\(^1\) To consider semipermeable layers is a novel concept which appeared for first time in [19]
Contacts. Finally, there are two contacts, the front contact and the rear contact, and there is also technology challenges in improving them to enhance solar cell performance. One important issue is the material this contacts are made of, which basic relies on its work function. The idea is that one wants to have the best carriers collection possible, therefore the contacts need to be as near to Ohmic contact as possible, which basically means that the work function of the contact material have to be equal to the electron affinity of the neighbor material. Figure 1.3 shows two cases of metal-semiconductor junction where a barrier is induced since the work function of the metal does not match with the electron affinity of the semiconductor.
In the first case (a) the electron affinity of the semiconductor is lower than the work function of the metal, thus, a barrier for electrons is induced. In the second case (b) is the opposite case where a barrier for holes is induced.

Once a suitable material is chosen, for each contact, there are other technological issues. The front part of the cell have to be transparent so the light reaches the layer in which the carrier generation is supposed to take place. Since the metal is not transparent, it have to be distributed such that it shades as less as possible (Figure 1.4 shows a pattern of a typical front contact of an experimental prototype solar cell). Notice that one of the busbar ends is thicker so that it can be contacted with a metallic tip when the cell is going to be characterized and the other end is thinner to reduce the shadow.
1.1.3 Recombination

Crystalline silicon wafers used in photovoltaic (PV) exhibit a highly ordered structure with very few number of defects so charge carrier mobility is as high as possible. This is because Silicon atoms adopt a ........ structure in which the atoms are in stable structure, however at the surface, the atoms are stressed thus defects appear. This defects are energy states that trap charge carriers reducing the efficiency of the solar cell. Reducing this surface recombination is one way to improve crystalline silicon solar cell performance. In the Section 1.3 a solution to reduce it is discussed (passivation layers).

1.2 Electrical characteristics

1.2.1 The ideal solar cell

In this section the basic parameters of solar cells are defined. The ideal solar cell electrical behavior can be reproduced by the electrical circuit shown in Figure 1.5. Therefore it is characterized by its I-V curve (Figure 1.6) which follows the next equation.

\[ I = I_{ph} - I_0 \left( e^{\frac{qV}{k_B T}} \right) \]  

(1.1)

Being \( I_{ph} \) the photogenerated current, \( I_0 \) the dark saturation current, \( V \) the applied voltage between the contacts, \( q \) the electron charge, \( T \) the absolute temperature, \( k_B \) the
Boltzmann constant. The I-V characteristic of an ideal solar cell is represented in Figure 1.6.

Figure 1.5: Equivalent circuit for an ideal solar cell is represented by the full line. Dotted line show the non-ideal components [14]

Figure 1.6: (a) Electrical current and (b) power as a function of applied voltage for an ideal solar cell [14]
There are 2 important parameters shown in Figure 1.6, short circuit-current $I_{sc}$ and open-circuit voltage $V_{oc}$. In the ideal case, $I_{sc}$ is equal to $I_{ph}$ and $V_{oc}$ is given by

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{I_{ph}}{I_0} + 1 \right).$$

(1.2)

As Figure 1.6, the maximum power is obtained when voltage and current take the values of $V_m$ and $I_m$ respectively. The fill factor $FF$ is defined by

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} = \frac{P_{max}}{V_{oc} I_{sc}}. \quad (1.3)$$

$FF$ is highly related to the efficiency of the cell which is the ratio between the input light power ($P_{light}$) and the output electrical maximum power $P_{max}$

$$\eta = \frac{P_{max}}{P_{light}} = \frac{P_{max}}{E \times A} = FF \frac{V_{oc} I_{sc}}{E \times A}. \quad (1.4)$$

$E$ is the input light power per unit area, $A$ is the area of the solar cell.

### 1.2.2 Solar cell in practice

The I-V characteristics for real solar cells are slightly different from the ideal one. As one can see in the equivalent circuit for the non-ideal case, a two-diode model with both serial and shunt resistances is used (Figure 1.5). Then the I-V equation is given by

$$I = I_{ph} - I_{01} \left( \exp \frac{V + IR_s}{k_B T} \right) - I_{02} \left( \exp \frac{V + IR_s}{2k_B T} \right) - \frac{V + IR_s}{R_p} \quad (1.5)$$

The changes in I-V plot due to $R_s$ and $R_p$ are shown shown in Figure 1.7. Notice how a non-ideal solar cell has a lower $P_{max}$ thus a lower efficiency $\eta$. 


1.3 Technologies

Since the observation of the photovoltaic effect in 1939, so many different type of solar cells have been created. Figure 1.8 displays the development of solar cell efficiency from 1975 to 2015. There are four main groups which are represented with different colors. We are only interested in crystalline solar cells, specifically amorphous silicon heterojunction solar cells which in 2014 reached the high efficiency of 24.7% [22]. Although there are solar cells with higher efficiencies, they use technologies which are not able to be fabricated at a big scale.
1.3.1 Crystalline silicon solar cells

Also called conventional solar cells, they are based on crystalline silicon. The advantages of this devices is that they have a high charge carriers mobility and a large lifetime compared with other materials based solar cells. One of the drawbacks is that the crystalline structure is very stable at the bulk but it is not at the surface, thus a lot of defects appear there creating a high recombination surfaces which means charge carrier loses. This kind of solar cells exhibit a p-n structure that is fabricated starting from a p-doped (n-doped) crystalline silicon wafer followed by a creation of a n-doped (p-doped) layer by diffusion of the doping material at a high temperature (about 1000°C). This is a slow and expensive process, for this reason other technologies are being researched.

1.4 Passivation layers

As it is introduced in Subsection 1.1.3, passivation layers are used to reduce the surface defect density in order to increase the solar cell efficiency.

Initially, the fist idea was to use dielectric surface passivation layers, such as SiO₂, on the front side of the cell [7]. Then the surface recombination becomes significantly lower but metallic contacts still need to be directly contacted to the silicon wafer through the
isolator layer as shown in Figure 1.9. Therefore, recombination at the metal-semiconductor interface remains a problem due to the direct contacts.

Figure 1.9: Sketch of Crystalline solar cell with a SiO$_2$ passivation layer [7]

1.5 HIT silicon solar cells

The most successful option to solve the recombination problem is to have a doped hydrogenated amorphous silicon thin film (a-Si:H) on a doped crystalline silicon wafer forming a p-n heterojunction [24]. However this structure exhibit a large interface state density since the a-Si layer is highly doped. To over come this issue, a thin buffer layer of intrinsic a-Si:H is deposited between the emitter and the wafer leading to a Heterojunction with Intrinsic Thin-layer (HIT) structure.

1.5.1 A-Si/c-Si Hetero-junction benefits

Apart from reducing the surface recombination, heterojunction solar cells provide more advantages. One of them is the increase of the open circuit voltage $V_{oc}$. This fact is due to the amorphous silicon higher bandgap. This phenomena can be deduced from equations that describes an ideal p-n junction presented below.

As one can see in Equation 1.2 the open-circuit voltage $V_{oc}$ depends on the saturation current $I_0$ that can be calculated from the saturation density current $J_0$ which is given by

$$J_0 = qn_i^2 \left( \frac{D_N}{L_N N_A} + \frac{D_P}{L_P N_D} \right).$$

(1.6)
$D_N$ and $D_P$ are the diffusion coefficients for electrons and holes, $L_N$ and $L_P$ are the diffusion lengths, $N_D$ and $N_A$ are the doping concentrations for donor and acceptor impurities respectively. In particular, the bandgap is related with the intrinsic level of charge carriers $n_i$ such that

$$n_i^2 = N_C N_V \exp\left[-\frac{E_G}{kT}\right].$$

(1.7)

Therefore, an increase of $E_G$ produces $J_0$ to decrease, resulting in a higher $V_{oc}$.

A-Si:H layers can be deposited in a low-temperature process ($<200^\circ$C), therefore, very thin wafers can be used without causing substrate warping which is another important advantage. Another advantage is that HIT solar cells present a better performance when temperature increases.

In short, HIT silicon solar cells provide a higher efficiency and a lower fabrication cost. Notice that in Figure 1.10 similar a-Si:H layers have been also implemented at the rear side of the cell to further improve the HIT solar cell [23].

![Figure 1.10: Sketch of the HIT solar cell developed by Sanyo with its band diagram [7]](image)

1.6 Transition-Metal-Oxide HIT solar cells

1.6.1 Transition-Metal-Oxides

Photovoltaic energy can still not compete in terms of price with conventional energy sources. Thus further price reductions are required. Transition-metal-oxide (TMO) are of great interest since they are cheap, non-toxic, abundant and provide new low-cost deposition methods. TMOs are suitable in terms of optical properties. However they exhibit
poor electronic properties such as short lifetime and low mobility of the excited charge carriers. Accordingly, TMO can not substitute current semiconductor materials used in PV but they can be used as permeable transport layers [19].

Permeable transport layers is a novel concept in photovoltaic which refers to a thin film that allows to pass through either electrons or holes, hence it improves the carrier collection. Adding two semi-permeable charge transport layers at both sides of the cell promote holes to be collected in one contact and electrons to be collected in the other one without having to create a p-n junction by doping processes. This enable the fabrication of solar cell devices without expensive processes involving toxic gases. Many examples of TMOs used are, $TiO_2$ and $ZnO$ as electron-transport layers [5], $NiO$ [20] $V_2O_5$ [8] $WO_3$ [13] and $MoO_3$ [11] as hole-transport layers.

1.6.2 TMO/c-Si heterojunction

One application of TMOs as a semipermeable charge transport layers is using them in a HIT Silicon solar cell as a substitute of the emitter layer. As it is explained in Subsection 1.5, in classical solar cells, the emitter layer is doped (in this case it would be p-type since the absorber layer n-doped) in order to get the p-n junction. However in this novel structure the emitter is substituted by a TMO layer which has not treated with a doping process, so there is no the typical p-n junction. New researches have reported that TMO layers as $MoO_3$ exhibit n-doped donor states [12]. The idea is that TMO HIT presents an n-doped layer on a n-doped c-Si wafer but it extracts holes as a p-doped layer would do. This phenomena dos not have a well demonstrated explanation, however, in this section a possible theory is exposed. The key point relies in the interface TMO/c-Si so let us see how the band diagram could be.

Mainly, three TMOs are used as hole transport layers in HIT crystalline silicon solar cells which are $MoO_3$, $V_2O_5$ and $WO_3$. Recent studies have measured the valence band (VB) and conduction band (CB) states of this TMO using Ultraviolet Photoemission Spectroscopy (UPS) and IPES Inverse Photoemission Spectroscopy (IPES)(Figure 1.11. Crystalline silicon n-doped layer band diagram is also shown in this figure in order to highlight the energy differences between them. Notice that due to the high electron affinity of all the TMOs, its Fermi level its much lower than the c-Si one.
Figure 1.11: Energy levels of three common used electron transport TMOs: \( MoO_3 \), \( V_2O_5 \), \( WO_3 \) and n-doped crystalline Silicon c-Si. VB and CB are the valence and conduction bands respectively, \( E_{VL} \) is the vacuum level and \( E_F \) is de Fermi energy level. Adapted [15]

Once the energy bands of both materials are known the question is how they would be in a junction. The key point is to see that in any junction, the difference between Fermi levels is what establish the curvature of the Energy bands.

In the classical crystalline silicon junction, the doping of each zone is what determines the Fermi energy levels since the electron affinities(EA) are the same. If we consider a p-n junction, the Fermi Energy level of the p-zone \( E_F^p \) will be lower than the Fermi Energy level of the n zone \( E_F^n \), therefore the electrons will diffuse to the zone with lower Fermi Energy level(form n-zone to p-zone), so the bands will be bended as represented in Figure 1.12. Notice that both zones energy bands have been bended since the electrons of n-zone have diffused to fill holes in p-zone.
In a-Si:H/c-Si heterojunction, there is an electron affinity difference between both zones but (p)a-Si:H Fermi Energy level $E_F^p$ is still lower than (n)c-Si Fermi energy level $E_F^n$, so the bands will be bended in the same way than the previous case.

However, if the EA of an n-doped material is high enough (as in the case of MoO$_3$), its Fermi energy level can be much lower than other n-doped material with a low EA like for example a (n)c-Si. Following the same argument, the electrons of the (n)c-Si layer (high Fermi energy level) will diffuse to the MoO$_3$ layer (low Fermi energy level) and the bands will be bended as in a p-n junction (see Figure 1.13).

Figure 1.12: Cystalline silicon p-n junction band diagram: (a) isolated (b) forming a junction
In fact it is not the same case as in a p-n junction for many reasons. Notice that \( MoO_3 \) bands are not bended and the whole depletion zone is on the c-Si. The proposed explanation is that since \( MoO_3 \) is a material with a high level of donor states the electrons that diffuse from (n)c-Si remain in the first few nanometers which mean that the bending is almost negligible. Nonetheless, other works represent \( MoO_3 \) junction with bended energy bands 1.14.

The second important aspect to comment is that in Figure 1.13 c-Si energy bands have been completely bended (\( \sim 0.9eV \)) until the point where Fermi level have reached the valence band. However the starting difference between Fermi energy levels of both materials is (\( \sim 2.7eV \)), so there is remaining energy that can not bend c-Si energy bands anymore. The proposed answer is that there is a charge surface density proportional to that remaining energy. The idea is the same as in a MOS FET transistor, when the gate voltage overcomes certain value where the semiconductor energy bands reaches a bending limit, a surface charge density appears in the semiconductor/oxide interface in order to balance the resting voltage.

All of this hypothesis are not demonstrated. Further research is required to understand \( MoO_3/(n)c-Si \) interaction.
1.6.3 TMO HIT solar cells in practice

Several researches have reported TMO HIT solar cells satisfying results [6] [3]. Figure 1.14 present the proposed band diagram of a $MoO_3$ HIT solar cell. We can see that they also consider a high band bending in the c-Si zone. The difference between this band diagram and the previous one is that in this one the energy bands of $MoO_3$ are bended. The whole idea is that $MoO_3$ is playing a similar role as a (p)a-Si:H layer. Notice that there are extra (i)a-Si:H layers between the (p) a-Si and c-Si layers whose role as a passivation layers has been explained before in Section 1.5.

Figure 1.14: Band diagram of (a) $MoO_3$ HIT solar cell and (b) amorphous silicon HIT solar cell. At the bottom of the diagram, the material of each layer is labeled. There are also indications labeling the different type of defect states in the bandgap of $MoO_3$ and (p)c – Si. Finally, the direction of flow for electrons and holes is indicated. The diagram is taken from [3]
Chapter 2

TMO HIT solar cell fabrication and characterization

2.1 Fabrication process

HIT solar cells based on three different TMOs have been fabricated in order to compare their performance. In this section, the fabrication process used is described which is the same for all the different TMO solar cells.

The fabrication process starts from a Float Zone (100) n-Si crystalline silicon wafer (1.5 $\Omega \cdot cm$, 280 $\mu m$ thick). The first step (which is optional since it is not clear if it...
improves the overall solar cell performance) is a random texturization of the wafer using alkaline etching\textsuperscript{1}. After, wafer have to be cleaned by RCA\textsuperscript{2} and 1\% HF dipping\textsuperscript{3}.

After the cleaning, the substrates were immediately loaded into a PECVD system to deposit a stack of layers on the rear side. This stack consist of 4 nm intrinsic a-SiCx:H (x 0.2) passivation layer, a 15 nm phosphorous-doped a-Si:H layer and a 80 nm a-SiCx:H (x 1) back reflector. Such a multilayer structure is able to provide an excellent back surface passivation and high internal reflection.

The following step is to laser-fire the rear side in order to obtain a locally-diffused point contacts which only fill a 0.5\% of the total area. Accordingly, a 99.5\% of the area is passivated thanks to the a-Si:H layer. Additionally the total rear contact resistivity is less than 1m\(\Omega\cdot cm^2\).

Once rear contact is finished, a second 1\% HF dipping is performed followed by the thermal evaporation of the TMO in the front side of the cell (pressure 8x10\(^{-6}\) mbar, deposition rate 0.2 Å/s, temperature according to each TMO evaporation point). Then the cell is briefly exposed to the air followed by the deposition of an ITO layer by RF magnetron sputtering.

Finally lithographic patterning of silver (50\(\mu\)m thick), for the front contact and metallization by e-beam evaporation of titanium (15nm) and aluminum (1\(\mu\)m), for the rear contact were done.

\section*{2.2 Characterization}

In this section we present the figures of merit of three different TMO/c-Si heterojunction solar cells and an a-Si/c-Si HIT solar cell in order to have it as a reference. Current-Voltage characteristic under illumination is shown in Figure 2.2a. One can see as all the TMO solar cells present similar performance and it is not so bad compared with the one of a-Si. Comparing the different TMO, \(V_{oc}\) exhibit slightly higher \(V_{oc}\) and \(J_{sc}\) thus higher efficiency.

Focusing on the EQE shown in Figure 2.2b we see that all oxides show a substantial improvement in the 300–600 nm range when compared to a-Si:H. Additionally, \(V_{oc}\) shows an additional absorption feature between 800 and 1000nm.

\begin{quotation}
\textsuperscript{1}A briefly description of this process is the following: crystalline silicon wafers are submerged in a solution that corrode its surface in a random way in order to increase is area.

\textsuperscript{2}Standard set of wafer cleaning steps in order to remove of the organic and ionic contamination. the acronym comes from Radio Corporation of America where Werner Kern was working when developed this procedure.

\textsuperscript{3}Procedure used to remove the silicon dioxide formed at the surface of the wafer.
\end{quotation}
Therefore, besides TMO solar cells exhibit lower efficiency, they present better EQE performance.

(a) Current voltage characteristic

(b) External Quantum efficiency

Figure 2.2: (a) current-voltage characteristic under illumination and (b) External Quantum efficiency for different TMO HIT solar cell compared with a-Si HIT solar cell

<table>
<thead>
<tr>
<th>Hole contact</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2O_x$</td>
<td>606</td>
<td>34.4</td>
<td>75.3</td>
<td>15.7</td>
</tr>
<tr>
<td>MoO$_x$</td>
<td>581</td>
<td>34.1</td>
<td>68.8</td>
<td>13.5</td>
</tr>
<tr>
<td>WO$_x$</td>
<td>577</td>
<td>33.3</td>
<td>65.0</td>
<td>12.5</td>
</tr>
<tr>
<td>(p) a-Si:H</td>
<td>685</td>
<td>34.4</td>
<td>77.6</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Figure 2.3: Basic parameters (open circuit voltage, short-circuit current, fill factor and efficiency) of our HIT solar cells based on three different TMOs

Notice that sometimes we refer to $MoO_3$ as $MoO_x$. That is because once evaporated and deposited on the cell, the composition is no longer $x=3$ but it is variable with an average of $x\sim 2.7$. This fact is the responsible of the donor defect states of these particular TMO [15]. The same happens with the other TMO.
Chapter 3

Simulation of an amorphous silicon HIT solar cell

The aim of the simulation part is to reproduce the three basic figures of merit of an a-Si HIT solar cell. There is not previous work to start from, thus, all modeling has to be performed. In order to have a reliable reference data, real solar cells manufactured in UPC electronic department have measured. All the simulations have been carried out using an electronic device simulation software called Silvaco ATLAS [16]. The details of the simulation are explained below (Section 3.1).

3.1 Description of the software

3.1.1 Electrical model

The simulation consist on solving the basic semiconductor equations in several points of the device properly placed of a discrete mesh. The equations involved are detailed below.

Poisson’s equation which relates the electrostatic potential $\varphi$ with the free space charge density $\rho_f$.

$$\nabla \cdot \varphi = -\frac{\rho_f}{\epsilon}$$

(3.1)

Carrier continuity equations for electrons $n$ and holes $p$

$$\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot \vec{J}_n + G_n - R_n$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot \vec{J}_p + G_p - R_p$$

(3.2)
Where $G$ are the charge carrier generation rate, $R$ is the recombination rate, $\vec{J}$ the current density and $q$ the electron charge.

$\vec{J}_n$ and $\vec{J}_p$ are computed using the Drift Diffusion Model whose equations are

$$\vec{J}_n = qn_\mu n \vec{E}_n + qD_n \nabla n$$
$$\vec{J}_p = qn_\mu p \vec{E}_p - qD_p \nabla p$$

(3.3)

$\mu_\mu$ $\mu_p$ are the mobilities for electrons and holes, $E_n$ $E_p$ are, electron and hole concentrations are computed using the Boltzmann approximation

$$n = n_{ie} \exp \left[ \frac{q(E - E_{Fn})}{kT} \right]$$
$$p = n_{ie} \exp \left[ -\frac{q(E - E_{Fp})}{kT} \right]$$

(3.4)

$E_{Fn}$ $E_{Fp}$ are the Quasi-Fermi levels and $n_{ie}$ is the intrinsic charge carrier density which in Boltzmann approximation follows the next equation

$$n_{ie} = \sqrt{N_C N_V} \exp \left( \frac{-E_g}{2kT} \right)$$

(3.5)

$N_C$, $N_V$ is the effective density of states of conduction and valence bands respectively.

### 3.1.2 Optical model

ATLAS also simulate optoelectronic materials. The optical model can be divided into two parts. The first one is the optical ray trace using real component of refractive index to calculate the optical intensity at each grid point. The second part is the computing of absorption or photogeneration using the imaginary component of refractive index to calculate a new carrier concentration at each grid point.

To begin with, a light beam incident on the device is defined. Then, depending on the angle of incidence, the program will compute the transmitted and reflected beams in each interface between different materials. Therefore defining the index of refraction of each
material is a crucial point in the optical simulation. In this work, index of refraction data of each material has been taken from ATLAS database.

ATLAS uses Fresnel equations to compute the light propagation through the device

\[ E_r = \frac{n_2 \cos \theta_i - n_1 \cos \theta_t}{n_1 \cos \theta_t + n_2 \cos \theta_i} E_i \quad (\text{TE polarization}) \]

\[ E_t = \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_t + n_2 \cos \theta_i} E_i \quad (\text{TE polarization}) \]

\[ E_r = \frac{n_2 \cos \theta_i - n_1 \cos \theta_t}{n_1 \cos \theta_t + n_2 \cos \theta_i} E_i \quad (\text{TM polarization}) \]

\[ E_t = \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_t + n_2 \cos \theta_i} E_i \quad (\text{TM polarization}) \]

\[ R = \left( \frac{E_r}{E_i} \right)^2 \quad (\text{TM polarization}) \]

\[ T = \left( \frac{E_t}{E_i} \right)^2 \frac{n_2 \cos \theta_i}{n_1 \cos \theta_i} \quad (\text{TM polarization}) \]

\[ \theta_r = \theta_i \]

\[ n_1 \sin \theta_i = n_2 \sin \theta_t \quad (3.7) \]

Where \( E_i \) is electric field of the incident wave, \( E_r \) is the field of the reflected wave, \( E_t \) is the field of the transmitted wave. \( R \) is the reflection coefficient, \( T \) is the transmission coefficient, \( n_1 \) is the refractive index on the incident side and \( n_2 \) is the refractive index on the transmission side.

Generation of charge carriers is computed using Equation 3.8.

\[ G = \eta_0 \frac{P\lambda}{hc} \alpha e^{-\alpha y} \quad (3.8) \]

\( P \) is the ray intensity factor, which contains the cumulative effects of reflections, transmissions, and loss due to absorption over the ray path. \( \eta_0 \) is the internal quantum efficiency,
which represents the number of carrier pairs generated per photon observed. The magnitude $y$ represents a relative distance for the ray in question. $h$ is Planck’s constant. $\lambda$ is the wavelength, $c$ is the speed of light and $\alpha$ is the absorption coefficient.

ATLAS also have different solar spectrum data files. In this simulation AM1.5$^1$ has been used.

### 3.2 Modeling

First of all, literature research is required in order to know how to model the different parts of the cell. The structure of the amorphous silicon HIT solar cell that has been simulated is represented in Figure 3.1. In the following sections, the different layers of the structured are analyzed and the models used are discussed.

![Figure 3.1: Structure of a HIT amorphous silicon solar cell](image)

#### 3.2.1 First simplification: rear contact

The structure of our solar cell is quite unusual since its rear part does not have a doped layer as a hole transport layer but it have a laser-fired contact in which aluminum has diffused into c-Si wafer. Probably it is the most complex part of the cell in terms of geometry. However, it can be simplified while maintaining its important contributions in

---

$^1$The air mass coefficient defines the direct optical path length through the Earth’s atmosphere. AM1.5 is almost universal when characterizing terrestrial power-generating panels.

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the cell behavior. For example, the role of the first amorphous silicon layer is to passivate the recombination of charge carriers at the c-Si surface, thus it can be substituted by a low recombination rate boundary condition. Amorphous silicon carbide layer has the main role of a reflective layer, but it is almost an isolator, so it can be removed taking into account that the light will be reflected at that boundary. Finally, the punctual contacts can be modeled as surface contacts in the c-Si wafer, in fact the front finger contact is taken as a metallic surface as well (considering the appropriate contact resistance). In short, the whole rear part of the cell is substituted by two boundary conditions and a surface contact as represented in Figure 3.2

![Figure 3.2: Structure of a HIT amorphous silicon solar cell with the simplified rear contact](image)

**3.2.2 Simulation domain and discretization**

Common research solar cells have an area of about 1 x 1 cm$^2$ and are about 300$\mu$m thick, however, due to their high symmetry, the simulations can be reduced to a representative portion of the cell. In this case, the domain has been reduced into a portion which contains one of the finger of the front contact and half of the distance between fingers of non-contacted surface. The section is shown in Figure 3.3 and its size is 1.5mm and 300$\mu$m thick.

Sometimes this kind of simulations are performed in 2D for simplicity provided that there is a dimension in which the structure does not change. In our case, the structure is almost constant in the horizontal plane except for the rear punctual contacts. Nevertheless 2D section of the cell has been chosen as the simulation domain considering the rear contact as a finger maintaining the same ratio of contacted/non-contacted area as the real case. It is taken into account that this approximation could provide non-negligible errors [1].

The calculations of all the magnitudes involved in the simulation are computed in a finite number of points of the simulation domain. Therefore, An important aspect is a properly discretization in space of the domain in order to minimize errors achieving an
optimal computational cost. A mesh adapted to the structure of the cell has been defined which basically means that the density of nodes is higher in the interfaces between materials than in the other regions.

![Simulation 2D domain of a HIT amorphous silicon solar cell](image)

**Figure 3.3: Simulation 2D domain of a HIT amorphous silicon solar cell**

### 3.2.3 Crystalline silicon wafer

Our cell is based on a Float zone crystalline silicon wafer (1.5 Ω·cm, 280 µm thick). ATLAS provide many models for example related with the mobility and gap variations due to the temperature. Since we are interested on simulating in room temperature the model used only takes into account the following parameters.

\[
\begin{align*}
\mu_n &= 450 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\tau_n &= 2 \text{ ms} \\
NC300 &= 1.78 \times 10^{19} \text{cm}^{-3} \\
EG300 &= 1.1 \text{eV} \\
\mu_p &= 1300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\tau_p &= 2 \text{ ms} \\
NV300 &= 1.68 \times 10^{19} \text{cm}^{-3} \\
AFFINITY &= 4.05 \text{ eV}
\end{align*}
\]

\(\mu_n\) and \(\mu_p\) are the mobilities, \(\tau_n\) and \(\tau_p\) are the lifetimes for electrons and holes respectively, \(NC300\) and \(NC300\) are the densities of states of the conduction and valence bands respectively at a temperature of 300K.
The optical index of refraction is taken from the ATLAS database.

### 3.2.4 Amorphous silicon

Amorphous silicon structure is more complex than crystalline silicon, therefore a more specific model is required. The model proposed consists on defining a modified density of states starting from the crystalline silicon ones. The point is to add exponential decaying band tails and two Gaussian distribution mid-gap states (Figure 3.4) in the crystalline silicon density of states typical bands. It is known that the tail states are due to Si-Si weak-bond states and mid gap states due to Si dangling bonds [18]. This is the so-called defect-pool model [2] [25].

![Amorphous silicon density of states scheme](image)

**Figure 3.4: Amorphous silicon density of states scheme [17]**

ATLAS already have the option to add defect states following the model mentioned above. Here the details are reviewed. To begin with, the density of states function is defined as the sum of two tail states and two Gaussian states.

\[
g(E) = g_{TA}(E) + g_{TD}(E) + g_{GA}(E) + g_{GD}(E)
\]

(3.9)
subscript $T$ refers to a tail, $G$ to a Gaussian, $A$ to acceptor-like defects and $D$ to donor-like defects. Each term of the sum follow the next expressions

\[
\begin{align*}
  g_{TA}(E) &= NTA \exp \left[ \frac{E - E_C}{WTA} \right] \\
  g_{TD}(E) &= NTD \exp \left[ \frac{E_V - E}{WTD} \right] \\
  g_{GA}(E) &= NGA \exp \left[ - \frac{EGA - E}{WGA} \right]^2 \\
  g_{GD}(E) &= NGD \exp \left[ - \frac{E - EGD}{WGD} \right]^2
\end{align*}
\] (3.10)

Where $NTA$, $NTD$, $NGA$, $NGD$ determines the height and $WTA$, $WTD$, $WGA$, $WGD$ fix the width of the corresponding functions.

The probability of occupation for each density of states is the following

\[
\begin{align*}
  f_{TA}(E,n,p) &= \frac{\nu_n \ SIGTAE \ n + \nu_p \ SIGTAH \ n_i \exp \left[ \frac{E_i - E}{kT} \right]}{\nu_n \ SIGTAE \ (n + n_i \exp \left[ \frac{E_i - E}{kT} \right]) + \nu_p \ SIGTAH \ (p + n_i \exp \left[ \frac{E_i - E}{kT} \right])} \\
  f_{GA}(E,n,p) &= \frac{\nu_n \ SIGGAE \ n + \nu_p \ SIGGAH \ n_i \exp \left[ \frac{E_i - E}{kT} \right]}{\nu_n \ SIGGAE \ (n + n_i \exp \left[ \frac{E_i - E}{kT} \right]) + \nu_p \ SIGGAH \ (p + n_i \exp \left[ \frac{E_i - E}{kT} \right])} \\
  f_{TD}(E,n,p) &= \frac{\nu_p \ SIGTDH \ p + \nu_n \ SIGTDE \ n_i \exp \left[ \frac{E_i - E}{kT} \right]}{\nu_n \ SIGTDE \ (n + n_i \exp \left[ \frac{E_i - E}{kT} \right]) + \nu_p \ SIGTDH \ (p + n_i \exp \left[ \frac{E_i - E}{kT} \right])} \\
  f_{GD}(E,n,p) &= \frac{\nu_p \ SIGGDH \ p + \nu_n \ SIGGDE \ n_i \exp \left[ \frac{E_i - E}{kT} \right]}{\nu_n \ SIGGDE \ (n + n_i \exp \left[ \frac{E_i - E}{kT} \right]) + \nu_p \ SIGGDH \ (p + n_i \exp \left[ \frac{E_i - E}{kT} \right])}
\end{align*}
\] (3.11)

Where $\nu_n$ is the electron thermal velocity and $\nu_p$ is the hole thermal velocity, $n_i$ is the intrinsic carrier concentration. $SIGTAE$ and $SIGGAE$ are the electron capture cross-section for the acceptor tail and Gaussian states respectively. $SIGTAH$ and $SIGGAH$
are the hole capture cross-sections for the acceptor tail and Gaussian states respectively and \( SIGTDE, SIGGDE, SIGGDH, \) and \( SIGGDH \) are the equivalents for donors states.

Finally, other parameters like charge carrier mobilities \( \mu_n, \mu_p, \) energy band gap \( E_g \) and electron affinity also must be modified.

Many variations have been considered based on ATLAS database examples and works where amorphous silicon has been simulated [4]. The final chosen parameters are the following

\[
\begin{align*}
\mu_n &= 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\tau_n &= 100 \text{ ns} \\
NC300 &= 2.5 \cdot 10^{20} \\
EG300 &= 1.8\text{eV} \\
\mu_p &= 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \\
\tau_p &= 1 \text{ ns} \\
NV300 &= 2.5 \cdot 10^{20} \\
AFFINITY &= 3.8 \text{ eV}
\end{align*}
\]

\[
\begin{align*}
NTA &= 1 \cdot 10^{21} \text{ cm}^{-3}\text{eV}^{-1} \\
NTD &= 1 \cdot 10^{21} \text{ cm}^{-3}\text{eV}^{-1} \\
NGA &= 5 \cdot 10^{19} \text{ cm}^{-3}\text{eV}^{-1} \\
NGD &= 1 \cdot 10^{17} \text{ cm}^{-3}\text{eV}^{-1} \\
EGA &= 0.7 \text{ eV} \\
WTA &= 0.03 \text{ eV} \\
WTD &= 0.06 \text{ eV} \\
WGA &= 0.23 \text{ eV} \\
WGD &= 0.23 \text{ eV} \\
EGD &= 1.22\text{eV}
\end{align*}
\]

\[
\begin{align*}
SIGTAE &= 1 \cdot 10^{-17} \\
SIGTDE &= 1 \cdot 10^{-15} \\
SIGGAE &= 2 \cdot 10^{-16} \\
SIGGDE &= 2 \cdot 10^{-15}
\end{align*}
\]

\[
\begin{align*}
SIGTAH &= 1 \cdot 10^{-15} \\
SIGTDH &= 1 \cdot 10^{-17} \\
SIGGHA &= 3 \cdot 10^{-15} \\
SIGGDH &= 1 \cdot 10^{-15}.
\end{align*}
\]

### 3.2.5 Indium Tin Oxide layer

Indium Tin Oxide (ITO) is a material widely used in electronics. It is similar to a TMO even thought it is not used as emitter layer like \( \text{MoO}_3 \) but as a front contact. The reason is that ITO exhibits a low resistivity (\( \sim 10^{-4}\Omega \cdot \text{cm} \)) compared with other TMOs (\( \text{MoO}_x \sim 10^4\Omega \cdot \text{cm} \)) and its bandgap is high enough (\( \sim 3.8\text{eV} \)) not to absorb the light from the solar spectrum. So it seems to be the best option to contact the whole solar cell front area without blocking the incoming light, then it is enough with a distributed metal
contact to have a low the total serial resistance\(^2\) as explained in Section 1.1.2.

Apart from the good conductivity and the transparency, the work function is crucial to determine if a material can be a good contact or not. In this case the work function of ITO is roughly 4.7\(eV\) and the (n)a-Si:H electron affinity is around 3.8\(eV\) so theoretically, there should a barrier of 0.9\(eV\) in their interface which means that ITO is not a good contact at all. However, there is a research that study (p)a-Si:H thin films sputter deposited on ITO and they conclude it forms an ohmic contact and it is due to interface defects \([10]\). Therefore it is not clear how exactly is the ITO/(p)a-Si:H real interaction.

To begin with, in the simulation ITO have been modeled as a high doped semiconductor \((10^{20} cm^{-3})\) with a high bandgap energy \((3.7eV)\) and a high electron affinity\((4.7eV)\). What is observed is that the current is too low due to an energy barrier between ITO and (n)a-Si:H which is blocking electrons to be collected in the front contact (as one would expect from the above paragraph explanation).

In short, the problem is that ITO is not acting as an ohmic contact but as a shottky contact\(^3\). The proposed simplification is to define ITO as a conductor with a resistivity of \(7.5 \cdot 10^{-4} \Omega \cdot cm\) (value taken from \([9]\)). ITO can be considered a conductor in terms of electrical behavior due to their high n-type electronic states. With this assumption, the fitting of the current-voltage characteristic have been excellent (Figure 3.5). Furthermore, in the simulation, the optical properties of each material are independent of the electric behavior, so the implication of defining a material as a conductor is that the program will consider the Ohm law to compute the current instead of solving the equations presented in subsection 3.1.

### 3.3 Results

Using all the parameters and models discussed in the previous section, External Quantum Efficiency (EQE) current-voltage characteristic in (dark and under illumination) has been reproduced. In this subsection we show and discuss the results obtained. Figure 3.5 shows the current-voltage characteristic in dark, Figure 3.6 display the current-voltage characteristic under illumination and Figure 3.7 shows the EQE for both cases.

---

\(^2\)In the solar cell circuit model there is a serial resistance which is the sum of all the the different materials contribution. The main part of this serial resistance is due to the contacts.

\(^3\)metal/semiconductor junction that exhibits an energy barrier which is proportional to the difference of the metal-vacuum work function and the semiconductor-vacuum electron affinity.
Figure 3.5: Real and simulated current-voltage characteristic in dark in (a) linear (b) logarithmic Y Axis.
Figure 3.6: Real and simulated current-voltage characteristic under illumination

Figure 3.7: External Quantum Efficiency measured (black) and simulated (red) results considering ITO

Current-voltage characteristic in dark have been properly reproduced. In Figure 3.5b the different current contributions explained in Section 1.2.2 can be easily distinguished.
interval (0.3V-0.5V) corresponds to the recombination exponential term, interval (0.5V-0.7V) corresponds to the ideal diode and (0.7V-1.0V) interval is determined by the serial resistance.

The first zone (0V-0.3V), simulated curve is slightly different from the real one. This zone is related to the shunt resistance term of the circuit model of the solar cell. The reason of the bad fitting in this zone could be that in the simulation there is not the possibility of taking into account a shunt resistance. From 0.3V to 1V, the curve has been accurately fitted.

EQE curve has not been so well reproduced. However we have hypothesis about how to improve it. The biggest difference lie on the zone 300nm-500nm. We know that this zone corresponds so the high energy part of the solar spectrum. We also know that this high energy waves are always absorbed in the first layer of a solar cell which in this case corresponds to the ITO layer, so in a real solar cell, this light is not exploit. However, the simulated EQE curve indicate that this light is being transformed into electric current. The reason is that ITO is not absorbing that part of the spectrum but silicon wafer does instead. The problem is that ITO has not been properly simulated in terms of optical properties, since it has been defined as a perfectly transparent material. The simulation result does not fit the real results in the others zones either so in conclusion, the optical modeling of the device has to be further improved.
CONCLUSIONS

Different TMO have been used as a hole transport layers in a crystalline silicon solar cell. This solar cells present substantial improvements in terms of low fabrication process. The results obtained in the characterization part shows that TMO are can substitute of amorphous silicon. Moreover they present better External Quantum Efficiency at the low wavelength part of the spectrum which is another promising feature. However further research is required to improve their efficiency. We have explained one hypothesis about the interaction between TMOs and crystalline silicon but there is a lot of work on better understanding it.

The results of the simulation part are only a first approach to the real case. As one can see in the previous modeling subsections, there are a lot of parameters to set in order to get this results. It is important to realize that only few of them are absolutely well known for the real solar cell. Therefore there is a lot of work in order to understand the effect of each parameter on the cell behavior and to decide their proper values which means that a lot of simulations have been performed for each different parameter and the results are not presented in this memory. All the parameters chosen to get the presented results would have to be discussed in depth to ensure that they are consistent which would require a lot of characterization experiments.

One important conclusion is to realize how difficult is to simulate such a complex device and to assess the reliability of the results. After all, even if the simulation can not be of any practical use, it is a very good exercise to get into the depths of the device, even of physics of the materials.
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