

**École polytechnique de Louvain**

# **Exploration of different materials for solar cells: hole selective layer and space radiation effects.**

Study of NiO and WO<sub>3</sub> as hole selective layer and  
effects of space radiation on three different solar  
cells

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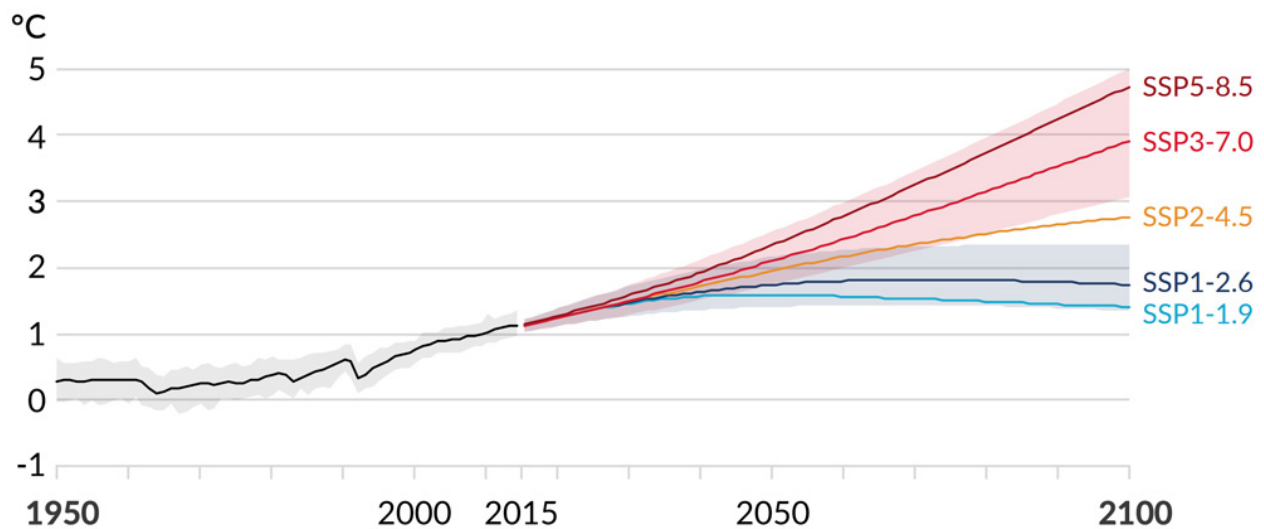


# Chapter 1

## Introduction

### 1.1 Context

The release of the sixth climate assessment report (AR6) from the Intergovernmental Panel on Climate Change (IPCC) has never been so clear: the planet is heating and human activities are the cause. If the greenhouse gases emissions are not reduced, the global mean temperature could rise over 4°C (see Figure 1.1).



**Figure 1.1:** Global surface temperature changes relative to 1850-1900, degrees C, under the five core emissions scenarios used in AR6. From IPCC (2021) Figure SPM.8a.

To reduce it, the world has to make a transition from fossil fuels (coal, oil and gas) which represent 84% of the world's energy in 2019[1], to low carbon emission energies: nuclear, hydro, solar, wind, etc.

Concerning the solar cell, many researches are conducted to improve the efficiency of the different technologies (silicon, CIGS, etc.) and approach their intrinsic limits. To do so, the researchers focus on several aspects like light reflection or reduction of electric losses. For the latter, carrier selective contacts (CSC) and passivation have received an increase interest over the years. If ideal, this solution suppress all the electrical losses at the interfaces solar cell/electrical contact. The record for a silicon solar cell used hydrogenated amorphous silicon to passivate the surface. It has achieved a carrier selective effect through doping and has an efficiency of 26.6%[2]. In comparison, the theoretical limit for a silicon-based solar cell is around 30%. However, the carrier selective effect through doping is not ideal due to parasitic absorption and recombination

inherent to the doped layer. To counter this effect, researchers have explored different materials to obtain a CSC but without doping. For example:  $\text{MoO}_3$ ,  $\text{WO}_3$  and  $\text{NiO}$ . When both contacts are CSC without doping, the structure is called dopant-free asymmetric hetero contact (DASH) solar cells. The efficiency record for this type of layout reaches 22.5% [3].

This thesis studies the  $\text{NiO}$  and  $\text{WO}_3$  as hole selective layers. A whole solar cell is not built. Instead, the electrical contact is studied through diverse measurements (IV, CV, lifetime), and the influence of one parameter is investigated (annealing temperature and thickness).

In a second time, the solar cell represents currently one of the only sources of energy in space and the most used. The other being nuclear with a radioisotope thermoelectric (RTG) generator. In the early age of space satellites, the silicon solar cell was preferred. However, it suffers greatly in the harsh space environment due to radiation, extremely low and high temperatures. Then, the GaAs cell was introduced thanks to its better performance, but it suffers from low efficiency. In order to raise it, the triple junction was created at the beginning of the 2000s. It consists of 3 junctions, gallium-arsenide (GaAs), gallium-indium-phosphor (GaInP) and germanium (Ge), stack on each other which greatly improve the efficiency. Nowadays, this type of cell has an efficiency of over 30% and are used in all the solar cells sent to space.

In conclusion, this thesis studies two subjects related to the solar cell. The first one has the aim to increase efficiency by decreasing the recombination at the interface. To do so, a passivation and a hole selective carrier layer are deposited on a simple structure and the interface is studied through IV, CV and lifetime measurement. The second one covers the performance degradation of a solar cell due to space radiation. To compare the impact on different technologies, three solar cells are irradiated: triple-junction gallium based, silicon and CIGS.

## 1.2 Thesis outline

To elaborate about these two subjects, this thesis is built in five chapters, starting with the introduction. The second part covers the theoretical concepts encountered. It starts with a description of a solar cell and explains the intrinsic and extrinsic losses. Then, the passivation and carrier selective layer are presented as a solution to increase the efficiency. Afterwards, the space environment is described with the degradation it causes on electronics and their different mechanisms. Finally, the methods to study the deterioration are presented, chosen, and the radiation parameters, like the energy and the time, are calculated.

The third chapter presents the different layouts and processes, with the parameters settings, done to obtain them. It develops the three solar cells studied before and after radiation, silicon, CIGS and triple-junction solar cell. It concludes with the details of the different types of equipment and measure used to characterise the samples and solar cells.

The fourth chapter presents and develops the results by starting with the characterisation of the samples (by XRD, XPS, etc.) to have their intrinsic properties. Then, the quality of the interface  $\text{Si}/\text{SiO}_2/\text{CSC}$  layer is investigated with CV and IV measurements. Finally, the damage due to the radiation of the 3 solar cells is assessed through dark IV/CV, light IV and noise measurement.

The last chapter concludes on the main results and proposes the future work that may be carried.

# Chapter 2

## Theoretical background

This second chapter introduces the different theoretical concepts encountered in this work. First, a brief description of how solar cell works is established. Then, its losses, intrinsic and extrinsic, are explained with a focus on the recombination mechanisms. This is followed with a explanation of three different techniques to reduce recombination at the interface: field-effect passivation, passivation and carrier selective layer. For the latter, different materials are proposed, and a definition of selectivity is developed. Afterwards, it is tested on a simple model of a solar cell to highlight the role of the various parameters.

Next, a section is dedicated to the radiation of solar cells which start with an explanation of the origin of radiation. Then, three degradation mechanisms are presented with examples and the impacted technologies. It concludes with the choice of the radiation source and the explication of the displacement damage equivalent fluence model. This model has allowed to determine the radiation parameters and to realise how long is to irradiate a solar cell.

### 2.1 Electrons-holes generation and losses

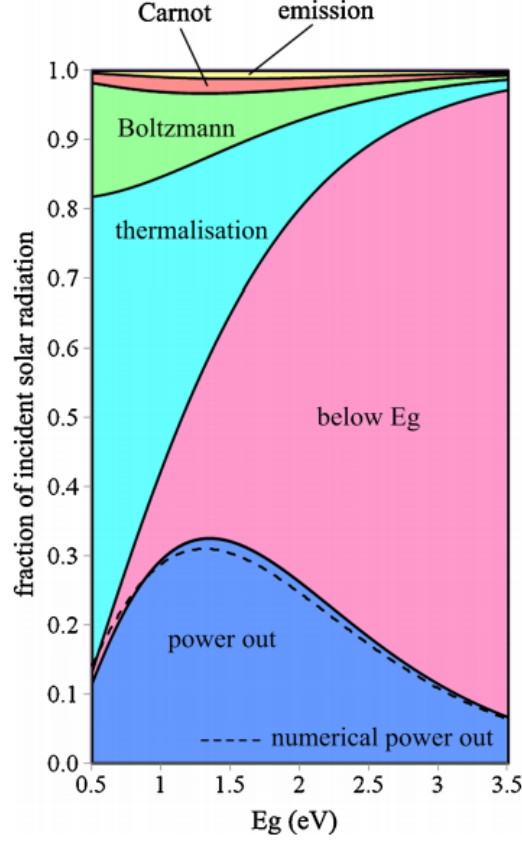
A solar cell is made of two types of semiconductors, called p-type and n-type. Together, it forms a PN junction. Some details are skipped, but when the sunlight hits the junction, an electron from the valence band can jump to the conduction band and becomes a "free-carrier". In response, a hole is left behind which is the creation of electron/holes pair. The energy that the negative carrier acquires has to be greater than the bandgap of the semiconductor.

Then, the electrons and holes generated go in opposite directions and "try" to reach the electrical contacts on each side of the junction, producing electricity. The more pairs arriving at their contact, the more energy is collected. However, different losses may reduce the efficiency of the solar cell.

The firsts are the intrinsic losses which are unavoidable. L. Hirst et al. [4] present 5 different mechanisms and their importance in function of the bandgap (see Figure 2.1).

- The power out: It is the maximal theoretical power. For a silicon-based solar cell ( $E_g = 1.14$ ), the maximal efficiency is around 30%.
- "Below  $E_g$ ". It is for the non-absorbed phonon with an energy below the bandgap. That is why multi-junction cells are developed: with different bandgap, it is freed from part of this constraint. Nevertheless, they are still confronted with the same problem described in this chapter.
- "Thermalisation". Since there is a strong interaction between the lattice phonons and the charge carrier, the latter will lose a part of its energy and heat the cell.

- The "Boltzmann" loss refers to an entropy generation due to the expansion of photon modes.
- The "Carnot" indicates the loss due to the conversion loss of thermal into electrical energy.
- "Emission" refers to spontaneous recombination of an electron/hole pair that will lose its energy by emitting light. It is also called radiative recombination.

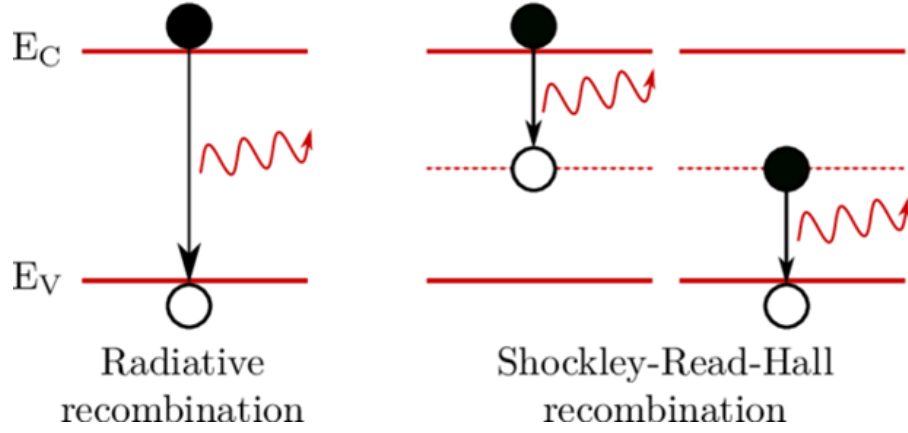


**Figure 2.1:** Intrinsic loss processes and maximum theoretical power out versus the bandgap ( $E_g$ ). From [4].

Afterwards, there are the extrinsic losses. It includes the dissipation of energy in the series resistance, leaks in the shunt resistance, etc. One mechanism of interest in this thesis is the non-radiative recombination. This process is similar to the emission describes above, but involves defects (see Figure 2.2).

Defects (also called traps) are a large concept that groups different phenomena. It is present in every crystalline material (like silicon) with dangling bonds, vacancies, dislocations, etc, and each will have a certain energy level with a type: neutral, donor (gives an electron) and acceptor (give a hole). Thus, even intentional doping can be considered as a defect.

These traps act as a recombination centre for the free electrons or holes that were photo-generated earlier. If they are recombined instead of being collected by the contacts, the energy accumulated from the phonon will be dissipated in heat, resulting in energy loss and efficiency. This represents the Shockley-Read-Hall (SRH) recombination mechanism.



**Figure 2.2:** Schematic illustration of the fundamental recombination mechanisms. Radiative recombination (left) is the inverse process of photon absorption. Shockley-Read-Hall recombination (right) means relaxation via defect induced intermediate energy levels. From [5].

## 2.2 Interface passivation

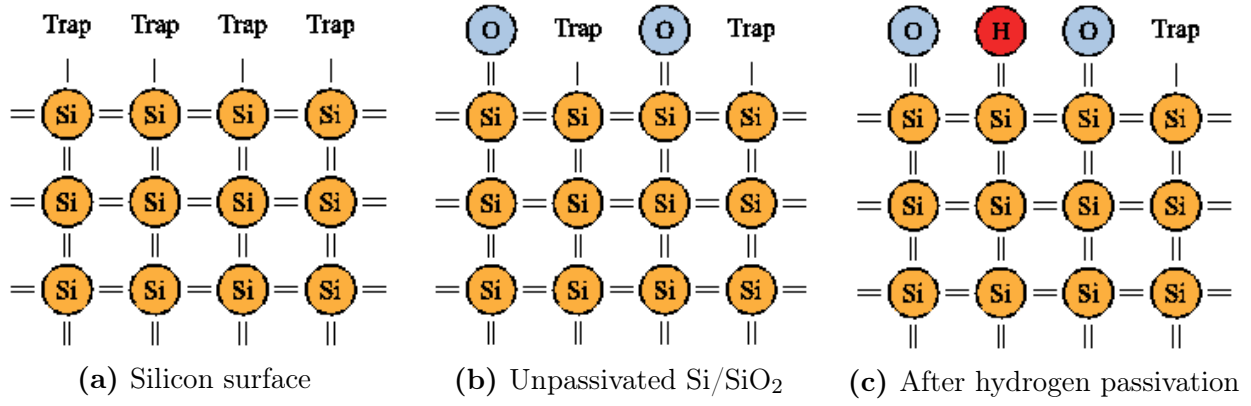
The majority of the defects are principally located at the junction interfaces with vacancies, dangling bonds and so on. Thus, the research is focused on reducing defects concentration and recombinations via 3 different techniques: passivative layer, carrier selective layer or field-effect passivation. However, the latter is not studied in this thesis. The working principle is to deposit a layer with an additional charge distribution creating an electrical field that will repulse the free holes (electrons) where the electrons (holes) are collected. By doing so, the carrier will recombine less and the efficiency is raised.

### 2.2.1 Passivation layer

To neutralise some defects at the interface, a thin dielectric layer may be deposited to interact with them. Many different parameters affect the choice like thermal stability, deposition temperature and interface passivation quality.

For a silicon-based solar cell, two different dielectrics are considered. The first is the thermally grown silicon dioxide ( $\text{SiO}_2$ ). This material is vastly studied and the different processes have been optimised. It can have a low surface recombination rate ( $\text{SRV} < 30 \text{ cm/s}$  for the best ones) due to low densities of interface traps ( $D_{it}$ ), i.e. defects. Even though it has great advantages, its uses in the industry are quite limited because of the high temperature needed ( $> 900^\circ\text{C}$ ) to grow it which may negatively impact the carrier lifetime. Consequently, other materials with low-temperature deposition are investigated, like silicon nitride ( $\text{SiN}$ ). However, other problems arise. Due to a large density of positive fixed charge, it leads to a float junction in the device that needs to be tackled.

Back to the  $\text{SiO}_2$  process, Figure 2.3 presents it. Before the  $\text{SiO}_2$ , one can see traps at the interface due to dangling bonds of silicon. Then, the oxide is grown and some silicon will link with oxygen atoms to form silicon oxide. However, as shown in Figure 2.3b, some silicon atoms still have dangling bonds. These are due to the size of the oxygen atoms that take up too much space. To passivate them, the wafer can be annealed with hydrogen. Because of its small size, the molecules will diffuse through the  $\text{SiO}_2$  and form  $\text{SiH}$ , passivating some of the remaining defects at the interface. Since the numbers of traps are diminished, the carrier lifetime is increased while the SRV and  $D_{it}$  are reduced.



**Figure 2.3:** (a) At the silicon surface, silicon atoms are missing and unpaired valence electrons exist, forming electrically active interface traps. (b) After oxidation, most interface states are saturated with oxygen bonds. (c) After annealing the surface with a hydrogen-related species, the amount of interface defects is further decreased. From [6].

### 2.2.2 Carrier selective layer

To further improve the efficiency, an other type of layer was considered: the carrier selective. The objective is the same as the field-effect passivation, repulse the electrons (or holes) to let the holes (or electrons) be collected by the contact and avoid any recombination while having a low resistivity for the latter.

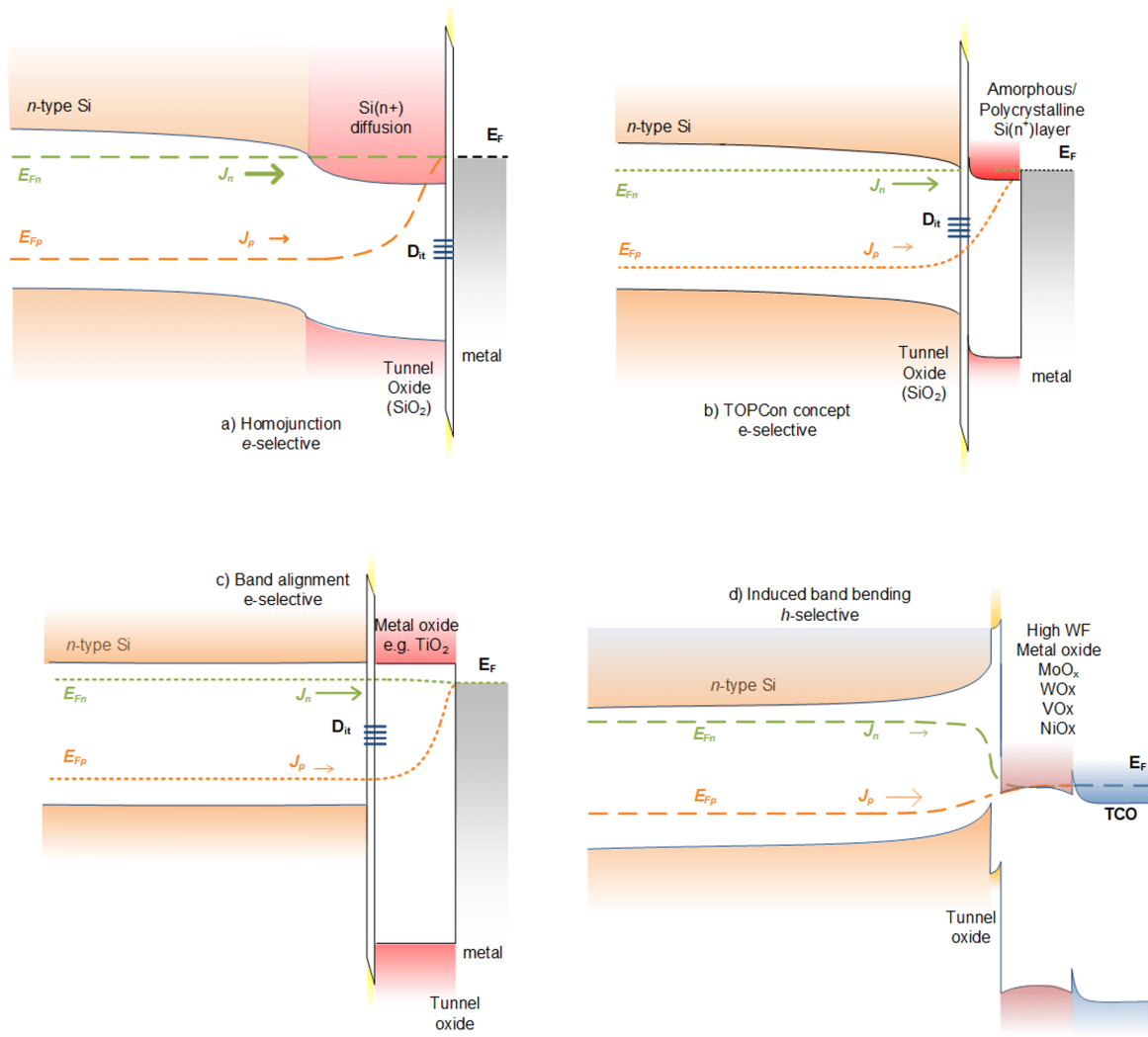
Figure 2.4 shows the band structure with the carrier current density for different carrier selectivity layers. The first one is done through a local change of doping called a diffused electron collector. It is the one dominating the silicon-based solar cell.

The three remained consist of a first passivation layer that will reduce the recombination due to defect, as explained in the previous section. The second layer has the role of contact selectivity and 3 different mechanisms are possible. It starts with the one used in heterojunction and TOPcon (Tunnel Oxide Passivated Contacts) structures. The layer deposited, doped (p for hole selective and n for electron selective) poly-silicon or amorphous silicon, has just an asymmetry in the conduction of holes and electrons.

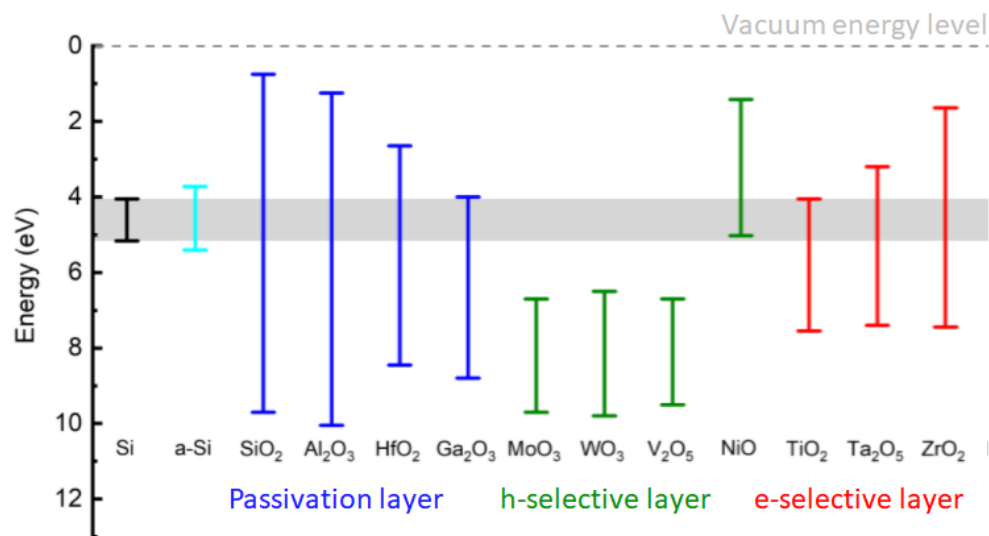
The next mechanism is based on band alignment. If the valence bands are aligned, it is electron selective, and if the conduction ones are, it is hole selective. The difference between the other band should be as high as possible to increase the selectivity. The materials used are varied but their work-function (WF) are generally either closed to the conduction band minimum for the e-selective, or closed to the valence band maximum for the h-selective [7].

For higher work-functions, band bending appears in the silicon due to a shift of the quasi-Fermi levels towards the valence band (hole contacts) or conduction band (electron contacts). It has a positive effect on selectivity.

Figure 2.5 presents the band alignment of different metal oxides compare to the silicon one. Different types of materials are also possible, like polymers or metal alloys [7].



**Figure 2.4:** Types of carrier selective contacts. From [8] adapted from [9].



**Figure 2.5:** Schematic illustration of the band alignment with Si of various metal oxides. From [8] adapted from [10].

Finally, Jan Schmidt et al. [11] tried to define selectivity, which was rather vague until now. The starting point is to assume that the selectivity is related to the different resistance of the majority (M) and minority (m) carriers. Then, let assume that the carrier selective has a total recombination rate,  $R(V)$  ( $\text{cm}^{-2} \text{ s}^{-1}$ ), which depends on the quasi-Fermi level splitting:  $V = (E_{Fn} - E_{Fp})/q$ . If so, the resistance for minority carriers is ( $q$  being the elementary charge):

$$\rho_m = \frac{V}{qR(V)}$$

As for the majority carrier, it is the contact resistance:

$$\rho_M = \rho_c$$

Thus, the ratio between the two is:

$$\frac{\rho_m}{\rho_M} = \frac{V}{qR(V)\rho_c} = \frac{V_{th}}{\rho_c \left( \frac{qR(V)}{e^{\frac{V}{V_{th}}} - 1} \right)} \frac{V}{V_{th} \left( e^{\frac{V}{V_{th}}} - 1 \right)} = S(V) g(V)$$

$S(V)$  is defined as the contact selectivity and  $g(V)$  a voltage-dependent factor with  $V_{th}$ , the thermal voltage. The selectivity can vary by several orders of magnitude. Therefore a logarithm is applied:

$$S_{10}(V) = \log_{10}(S(V))$$

The selectivity is now defined. However, it is voltage dependents which makes the comparison rather difficult. The most relevant is the maximum power point voltage ( $V_{mpp}$ ), but this varies for each cell.

Nevertheless, for highly doped surfaces, an important case according to the authors, is the recombination rate  $R(V)$  which follows the ideal Shockley diode equation with an ideality factor near 1 ( $J_0$  is the recombination current density).

$$R(V) = \frac{J_0}{q} \left( e^{\frac{V}{V_{th}}} - 1 \right)$$

It allows to make the selectivity parameter independent of the tension:

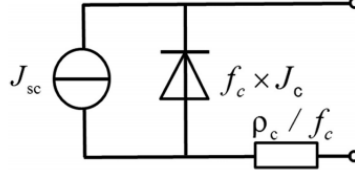
$$S = \frac{V_{th}}{\rho_c J_0}$$

To further analyse the impact of the selectivity, Rolf Brendel et al. [12] simulate a perfect silicon solar cell with just one contact. The circuit is shown in Figure 2.6 and is composed of 3 components with a new parameter,  $f_c$ , representing the areal fraction of the selective contact (due to the selectivity definition, it has no impact on it):

- A current source that generates an ideal current density ( $J_{sc}$ ) of  $43.6 \text{ mA/cm}^2$ .



- A diode representing the recombination in a selective contact given by the ideal Shockley diode equation
- A lumped series resistance representing the contact resistance  $\rho_c$  of the selective contact.



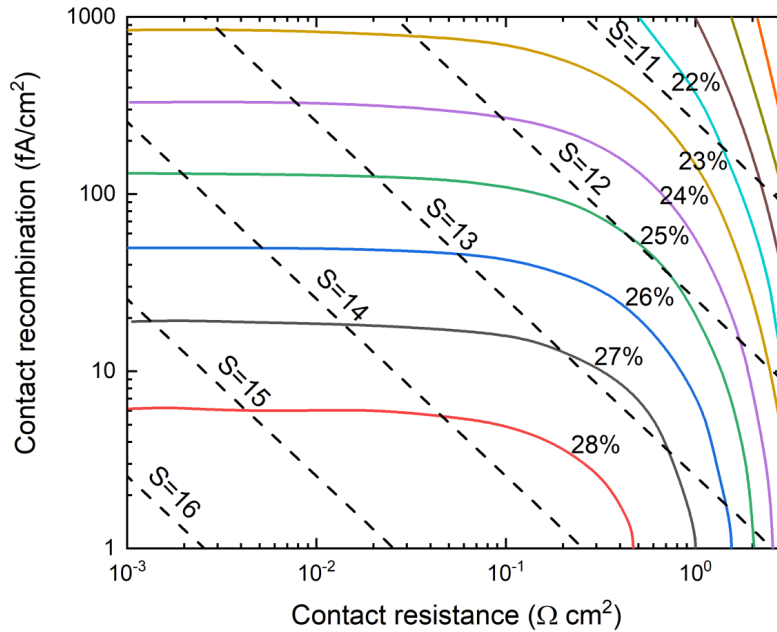
**Figure 2.6:** Equivalent circuit of a hypothetical solar cell characterized by a short circuit current density  $J_{sc}$ , a selective contact that is characterized by a recombination parameter  $f_c \times J_c$ , and a contact resistance  $\rho_c / f_c$ . Here,  $f_c$  denotes the areal fraction of the selective contact.

From [12]

Then, the efficiency is studied in function of the contact recombination and the contact resistance (see Figure 2.7). One of the first takeaways is that for certain selectivity (12 for example) a partial contact exist to maximise efficiency. At higher selectivity, a fraction close to one appears to be better.

A second takeaway is that, at low resistance, the recombination controls the efficiency. The trend changes at large  $\rho_c$  where it is the latter that will control it.

Unfortunately, this quantity was not used in this thesis due to the late discovery of the different documentations.

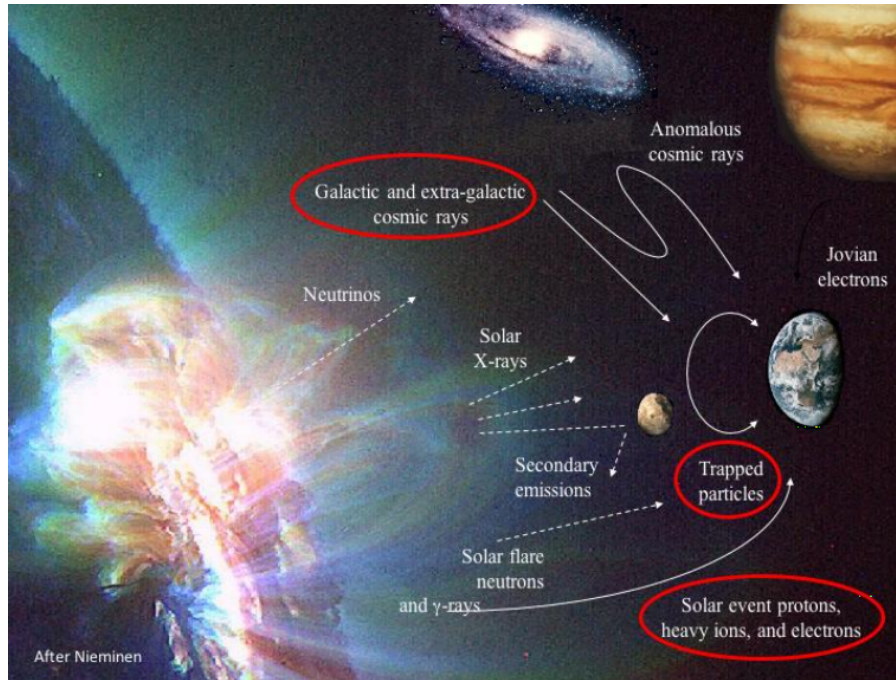


**Figure 2.7:** Upper limit efficiency of a silicon solar cell as a function of the minority carrier recombination current  $J_c$  and majority carrier contact resistance  $\rho_c$ . The dashed lines indicate iso-selectivity lines. Due to the definition of selectivity, it is possible to navigate on them by changing the ratio  $f_c$ . From [8] adapted from [12]

## 2.3 Radiation of solar cells

### 2.3.1 Space environment

The various electronics and humans sent to space are subject to a harsh environment due to an abundance of high energy particles. They come from different sources but stand out (see Figure 2.8)

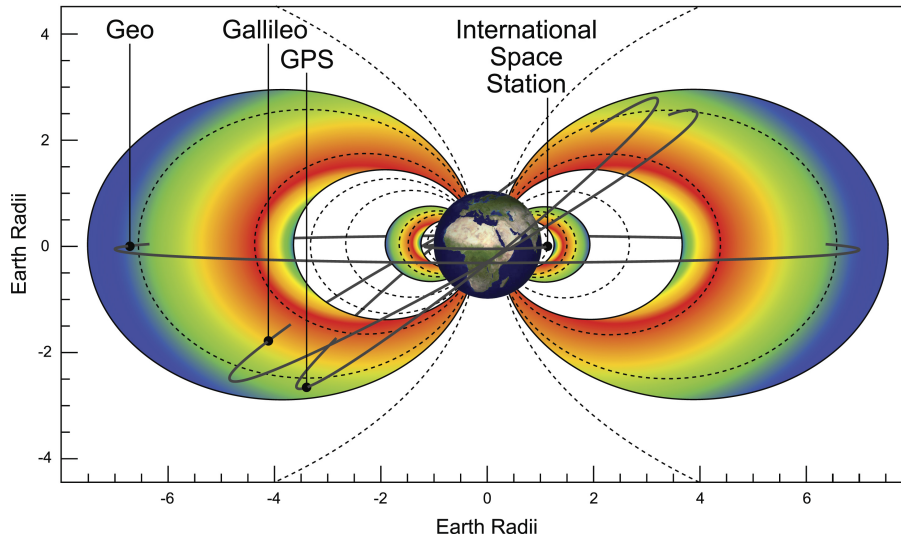


**Figure 2.8:** Schematics of the different sources of space radiation. The ones highlighted in red are the most important. From [13].

The first is the trapped particles, also called Van-Allen belts. Those are composed of protons and electrons coming from other sources trapped by the earth magnetic field. It is composed of an inner and outer belt (see Figure 2.9):

- The inner belt extends from 1000 to 12 000km. When the solar activity is considerable, it can go down to 200km. It dominates the absorbed radiation of the international space station (ISS) and low earth orbit (LEO) satellites. It is mainly composed of protons with an energy of up to 400 MeV.
- The outer belt covers a greater distance (i.e. 13 000 to 60000km) and impacts the navigation (GPS, Galileo) and geostationary satellites. It is populated mostly by electrons with an energy of up to 7 MeV.

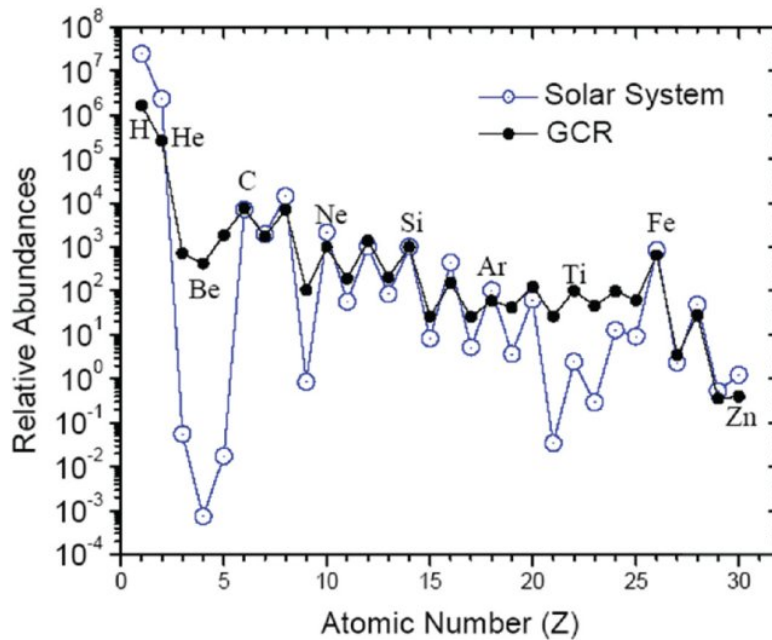
## Satellite orbits and the van Allen radiation belts



**Figure 2.9:** Van-Allen belts with different impacted orbits. From [14].

The second main source of radiation comes from solar events: coronal mass ejection and solar flares. These events eject protons, electrons and different heavier ions, all with a wide spectrum of energy. The solar flares depend on the activity of the sun, which has an 11 years cycle. As for the coronal mass ejections, they are unpredictable. Fortunately, the earth magnetic field shields a part of it, except at the poles. However, it can still cause damage to satellites.

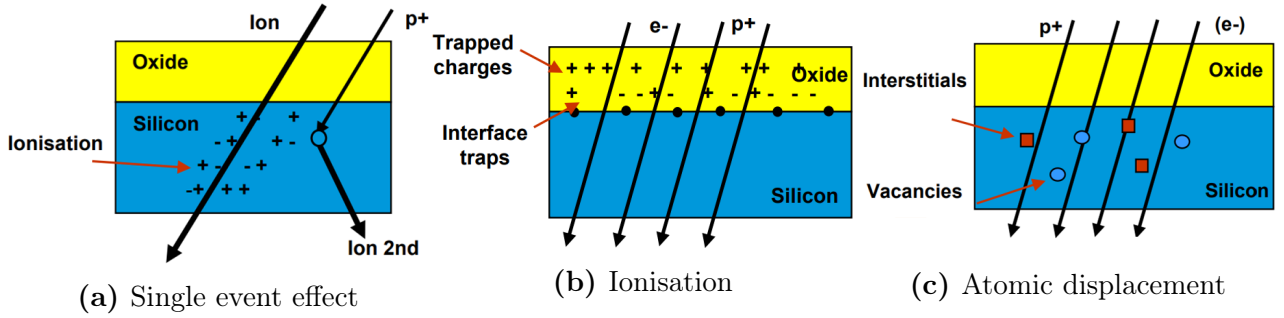
The third and last important phenomenon causing radiation is the galactic cosmic rays. It originates from outside the solar system. They are created probably in supernovas. Thus, nearly all particles are involved (see Figure 2.10), and they can be accelerated nearly at the speed of light with an energy reaching  $10^{20}$  eV (for comparison, the LHC is around  $10^{12}$  eV). The flux is around 4 particles/cm<sup>2</sup>/s. Like the solar events, the magnetic field offers some shielding.



**Figure 2.10:** Galactic cosmic ray relative abundances compared with the Solar System ones. The curves were normalized to Si= $10^3$ . From [15].

### 2.3.2 Degradation mechanisms

The radiation causes a lot of effects on the diverse electronics a satellite can contain. Three of the mains effects are shown in Figure 2.11.

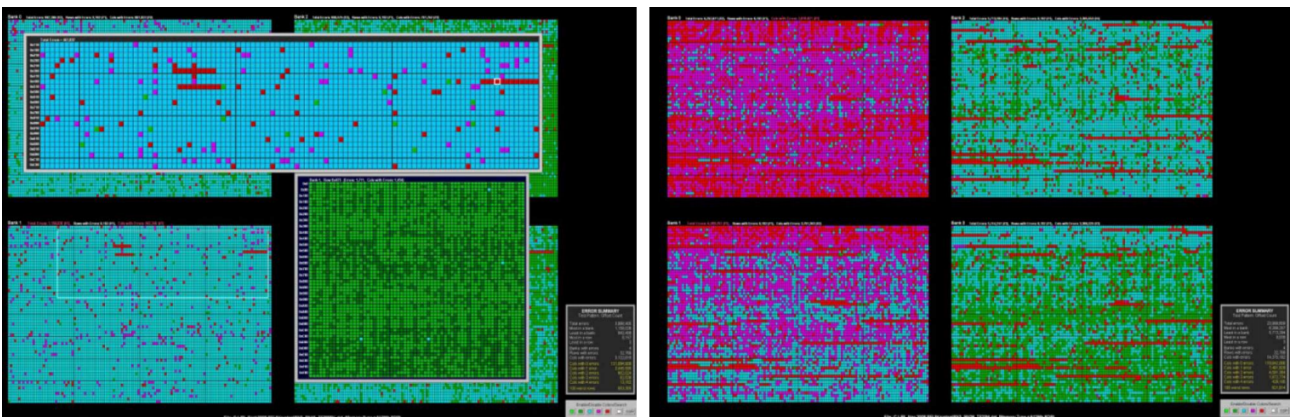


**Figure 2.11:** The three mains effects of radiation. From [13].

The first one is the single event effect (SEE). It is a 3 step processes:

- First, charges are generated in the device either direct, via Coulomb scattering, or indirect via nuclear scattering.
- Second, the charges are either collected by the circuit or they recombine.
- Finally, the system responds to what seems to be a signal.

The SEE is classified into different categories. All the devices are subject to the single event transient (SET). It is an impulse with a certain amplitude and duration. There is also the single event upset (SEU) which will corrupt the information stored in a memory. This can lead to a single event functional interrupt (SEFI) that will corrupt a datapath leading to a loss of operation (see Figure 2.12). In addition, some events can be destructive, like the single event burnout (SEB) that will destroy the device due to high current. To mitigate the different effects, redundancy is needed, as well as current limiting and auto memory reset.



**Figure 2.12:** Mapping errors for different cases in an SDRAM (typical on the left, extreme on the right), isolated green dots represent single errors, clusters consisting of 2 or more adjacent green dots are shown in red and indicate SEFI. From [13].



The second is the ionising effect. With the same mechanisms as the previous phenomenon, electron-hole pairs are generated in the oxide. If the device is biased, the carriers are swept, which leads to trapped charges and interfaces traps. It impacts the devices in different ways depending on the technology, process and bias conditions. Table 1 summarises it.

| Technology Category      | Effects                                                                                                           |
|--------------------------|-------------------------------------------------------------------------------------------------------------------|
| MOS                      | Threshold voltage shift<br>Decreased in drive current<br>Decrease in switching speed<br>Increased leakage current |
| BJT                      | $H_{fe}$ degradation                                                                                              |
| JFET                     | Enhanced source drain leakage current                                                                             |
| Analog microelectronics  | Change in offset voltage and offset current<br>Change in bias current<br>Gain degradation                         |
| Digital microelectronics | Enhanced leakage<br>Logic failure                                                                                 |
| CCDs                     | Increased dark current<br>Effects on MOS transistor elements                                                      |
| CIS                      | Same as CCD and change in pixel amplifier gain                                                                    |
| Quartz resonant crystal  | Frequency shifts                                                                                                  |

**Table 1:** Summary of the technologies and theirs TID effects.

The third and last one is the atomic displacement, also called displacement damage (DD) effect. If a particle has enough energy ( $>21$  eV for silicon), it can displace a Si atom of its lattice position, creating defects like vacancies and interstitials. Most of them will migrate and recombine ( $\approx 90\%$ , depending on the energy), and only a few will form stable defects. It will also impact the device depending on its technology. A non-exhaustive list is presented in Table 2. It shows that this is the main mechanism of degradation for a solar cell. To link with the previous section, the maximum power of a solar cell is reduced due to the defects which will increase the holes/electrons recombination.

| Technology Category   | Sub-category            | Effects                                                                                |
|-----------------------|-------------------------|----------------------------------------------------------------------------------------|
| Light-emitting diodes | LEDs (general)          | Reduced light power output                                                             |
|                       | Laser diodes            | Reduced light power output<br>Increased threshold current                              |
| Opto-couplers         |                         | Reduced current transfer ratio                                                         |
| Solar cells           | Silicon, GaAS, InP, etc | Reduced short-circuit current<br>Reduced open-circuit voltage<br>Reduced maximum power |
| General bipolar       | BJT                     | $h_{FE}$ degradation in BJTs, particularly for low-current conditions                  |
|                       | Diodes                  | Increased leakage current<br>Increased forward voltage drop                            |

**Table 2:** Summary of the technologies and theirs DD effects.

### 2.3.3 Radiation source and parameters

Thus, to test the three degradation mechanisms, the condition of radiation will be different. For example, the ionising and SEE are irradiated by cobalt 60. It is a byproduct of nuclear reactor operations and it produces two high energy gamma rays when it decays. The difference between the two will be the condition during the ionisation. For the SEE, the device, a memory for example, is irradiated while a program run in parallel to periodically fill and read the memory to measure the data corruption.

As for the solar cell, the atomic displacement (or displacement damage) is the dominant degradation mechanism. Its effects are mainly reproduced by protons or electrons irradiation produced by a cyclotron.

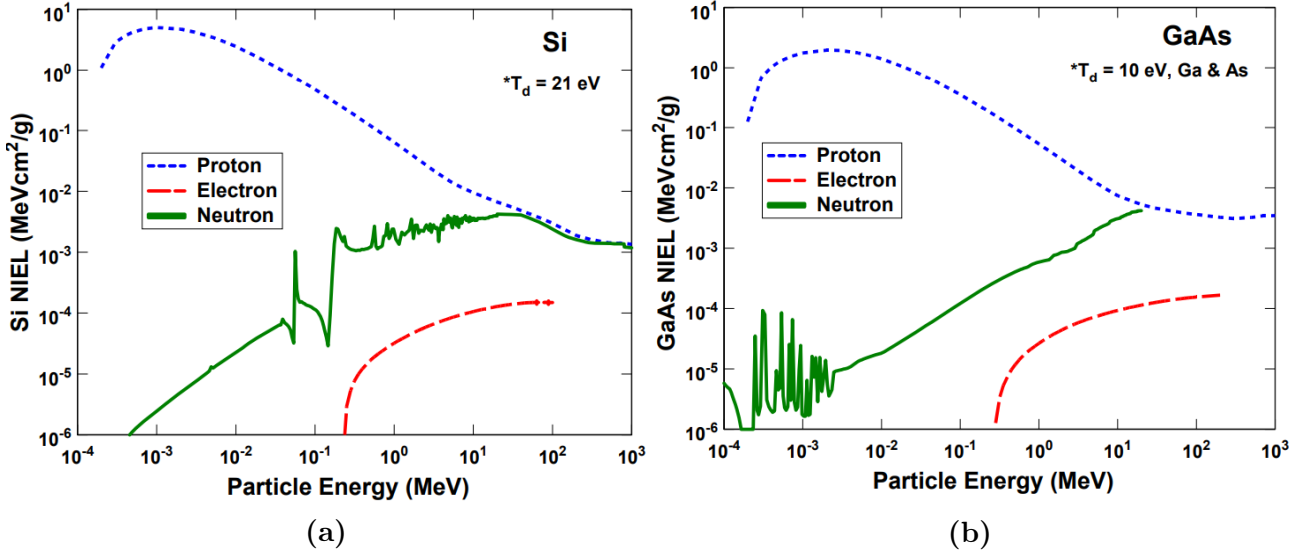
Now that the source is known, the energy and radiation time has to be determined and they are material dependent. The method used to set the parameters is the displacement damage equivalent fluence (DDEF) that gives the number of particles per area needed for irradiation following certain specifications. Since the damage is material and energy-dependent, it allows to define the parameters based on:

- The particle used (neutrons, protons or electrons)
- The energy of the particle.
- The shielding thickness (t).
- The total non-ionising dose (TNID).
- The non-ionising energy loss (NIEL).

The cyclotron to irradiate the solar cells uses protons with an energy between 10 to 60 MeV and a maximum fluence of  $2 \times 10^8$  ( $1/\text{cm}^2/\text{s}$ ).

For the TNID, it represents the total energy per gram (MeV/g) receive during the whole mission in space and it is material dependent. This work follows the specificity of the NeoSat missions (next-generation satellites platform initiative of ESA) that tabulates the TNID in function of the materials and its shield thickness for a duration of 15 years in space at a specific orbit. For the thickness, it is supposed  $100\mu\text{m}$  thick for all samples.

The NIEL is the rate at which energy is lost due to atomic displacements as a particle traverses a material. It is material, particles (neutrons, protons or electrons) and energy depend as shown in Figure [2.13](#).



**Figure 2.13:** Non ionising energy loss (NIEL) versus the energy for the silicon (a), gallium arsenide (b) and different particles. From [16].

Then, the displacement damage equivalent fluence is obtained with this relation:

$$\text{DDEF}(t,E) = \frac{\text{TNID}(t)}{\text{NIEL}(E)}$$

Then, the time in second is obtained with the fluence of the cyclotron ( $2 \cdot 10^8$  [1/cm<sup>2</sup>/s]).

$$\text{Time}(s) = \frac{\text{DDEF}(t,E)}{\text{Fluence}}$$

Table 3 presents the different steps for an energy of 10 and 60 MeV for a silicon and GaAs based solar cell.

|                               | 60 MeV               |                      | 10 MeV               |                      |
|-------------------------------|----------------------|----------------------|----------------------|----------------------|
|                               | Si                   | GaAs                 | Si                   | GaAs                 |
| TNID [MeV/g]                  | $1.77 \cdot 10^{11}$ | $1.48 \cdot 10^{11}$ | $1.77 \cdot 10^{11}$ | $1.77 \cdot 10^{11}$ |
| NIEL [MeV*cm <sup>2</sup> /g] | $3.52 \cdot 10^{-3}$ | $1.75 \cdot 10^{-3}$ | $7.86 \cdot 10^{-3}$ | $6.59 \cdot 10^{-3}$ |
| DDEF [1/cm <sup>2</sup> ]     | $5.02 \cdot 10^{13}$ | $8.46 \cdot 10^{13}$ | $2.25 \cdot 10^{13}$ | $2.24 \cdot 10^{13}$ |
| Time [h]                      | 69.72                | 117.46               | 31.27                | 31.19                |

**Table 3:** Summary of the calculations to have the radiation time with a proton energy of 10 and 60 MeV.

The results show a shorter irradiation time for 10 MeV due to a higher NIEL coefficient. Nevertheless, it is far too long for the Cyclotron organisation. Thus, the solar cell studied will be irradiated for just 1 hour each at 10 MeV with a fluence of  $2 \cdot 10^8$  1/cm<sup>2</sup>/s.

# Chapter 3

## Processes and methods

This chapter starts with a section about the processes. First, the different layouts used to do the different measurements are presented. Then, the different steps are detailed, like the  $\text{SiO}_2$  growth and oxide deposition. For the latter, the method to find the proper parameters and determine the deposition rate is elaborated. Afterwards, it is finished by presenting the metal layer oxidation technique and the different processes sheets.

It is then followed up by the presentation of the three different solar cells and their characterises.

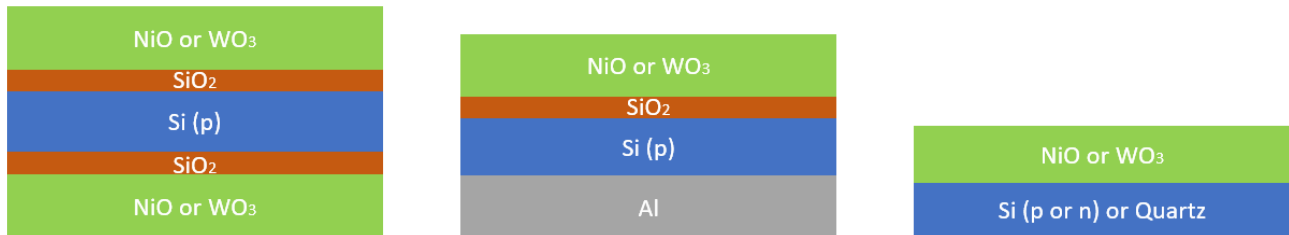
Finally, the different measures and equipment are detailed. Some are used to assess the samples and compare the results, done with different techniques or materials, found in the literature (CV, dark/light IV, noise and minority carrier). While other measures are to characterise what has been created in Winfab and their intrinsic properties (XPS, XRD and Hall effect and UV-visible)

### 3.1 Processes

To study different oxides as hole selective layer, two were selected based on the availability in the cleanroom. The first one is nickel oxide and the parameter studied is its thickness. The second one is tungsten oxide and the impact of different annealing temperatures were analysed.

In order to characterise the different properties (i.e. carrier lifetime, electrical and intrinsic properties), 3 types of samples were needed. Their layout are presented in Figure 3.1

For the minority carrier lifetime, the measurement is done by a quasi-steady-state photoconductance technique which imposes a symmetric stack of materials to measure the lifetime correctly. For the electrical measurement, a back contact is obviously needed. To measure the different intrinsic properties like the bandgap or the mobility, the oxide has to be deposited on either quartz or a highly doped wafer with the oxide's thickness greater than 50 nanometers.



**Figure 3.1:** From left to right: layout for the lifetime, electrical and intrinsic measurement



### 3.1.1 SiO<sub>2</sub> growth

The SiO<sub>2</sub> layer is 3nm thick and is thermally grown using the Koyo Thermo Systems by dry oxidation. The wafers start at 750°C under N<sub>2</sub> at 5 sccm and HCl at 0.5 sccm. Then, the temperature rises at a rate of 10°C/min to arrive at 950°C. After a standby of 10 minutes, 0.05 sccm of oxygen is released for 6 minutes to oxidize the wafer. Finally, the temperature decreases at 5°C/min to reach 750°C and the HCl is cut. The thickness and composition have been verified by XPS (see Section 4.1.1). This recipe has been developed by Yiyi Yan, a researcher from Jean-Pierre Raskin's team.



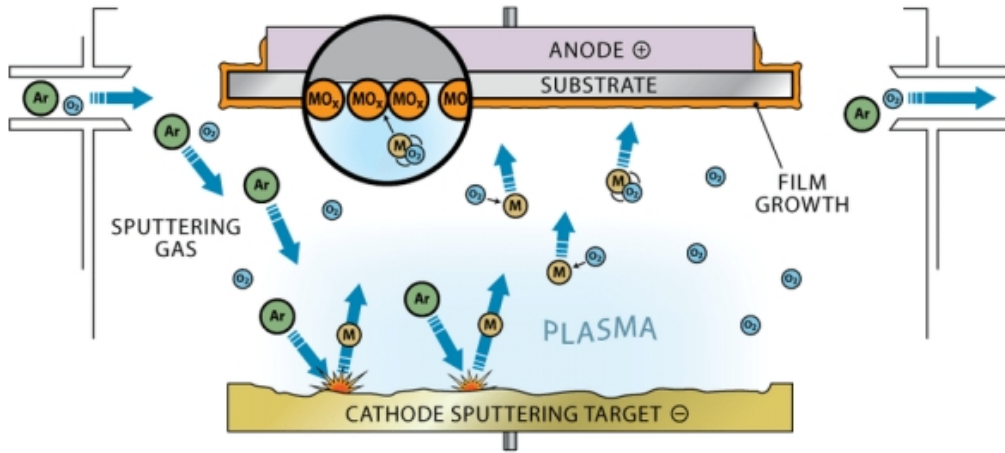
**Figure 3.2:** Koyo vertical furnace. It can hold 25 wafers of 3 inches.

### 3.1.2 Oxide deposition

There are a lot of different methods to deposit thin-film oxide (ALD, CVD, ...) [17], [18]. The one used in this work is DC reactive sputtering.

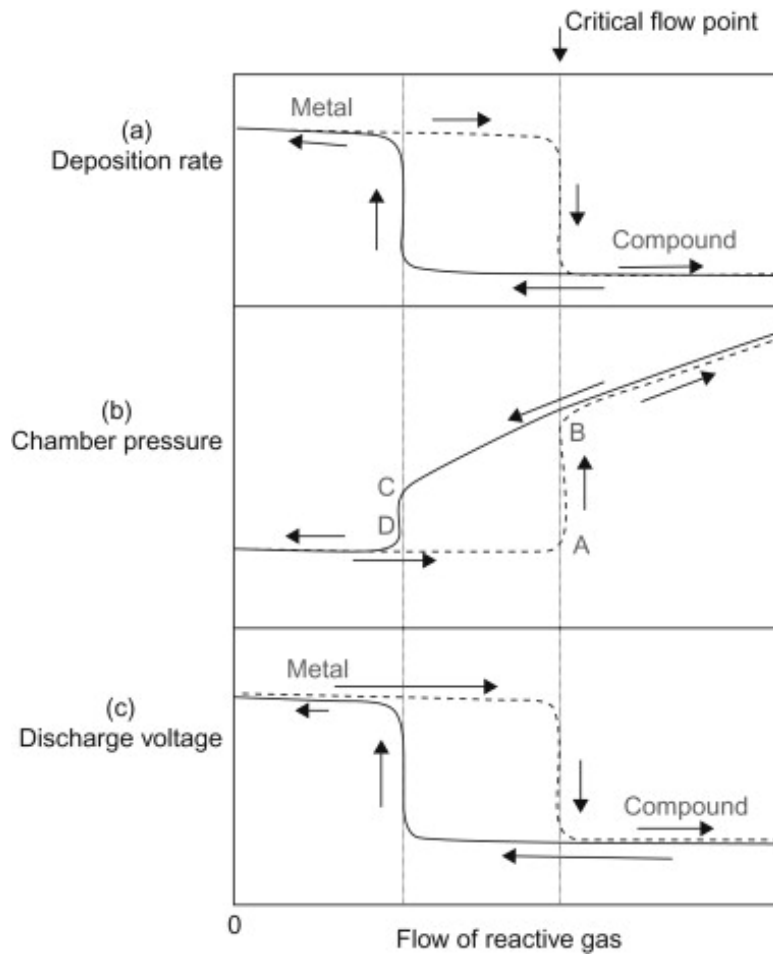
First, sputtering is a technique where a noble gas plasma, like Argon, is maintained in the deposition chamber. The ionised particle from the plasma will hit a cathode made of metal. By doing this, some metal will get off the cathode and go toward the wafer.

As for the reactive sputtering, the same concept is applied except that a reactive gas is released into the chamber. This gas will react with the metal particles that the plasma has ejected to deposit an oxide (O<sub>2</sub> is released) or nitride (N<sub>2</sub> is released) for examples. Figure 3.3 below illustrates the whole process with molybdenum as the target and O<sub>2</sub> as the reactive gas.



**Figure 3.3:** Schematic of the reactive sputtering. Image from [19].

To obtain an oxide with reactive sputtering, the flow rate of reactive gas has to be determined by looking at the voltage during the deposition while increasing the flow rate of reactive gas and keeping the other parameters constant (pressure and power). The voltage will have a sharp drop at the transition between metal or oxide deposition (see Figure 3.4). In this work, the direction taken is the dashed line (increasing the flow rate).



**Figure 3.4:** Representative hysteresis curves in reactive sputtering: (a) deposition rate, (b) chamber pressure and (c) discharge voltage as a function of reactive gas flow ( $O_2$ ) used in sputtering of a metal target (Al). Image from [20].

The reactive gas flow will also dictate the deposition rate (see Figure 3.4.a). Therefore, to have an oxide with also a good deposition rate, the working flow rate will be at the critical flow point. After the set of this parameter, the deposition rate can be measured.

### 3.1.3 The whole process

As explained at the start of this section, different type of samples are needed to conduct different measurements. However, they share the same silicon wafer from Sil'tronix. It was an n-type or p-type doubled polished 3-inch wafer with a resistivity of 1 to 10  $\Omega\cdot\text{cm}$  and a thickness of 340-380  $\mu\text{m}$ . They were processed using the floating zone (FZ) method that allowed them to have a high lifetime. For the fused quartz wafers, they were also doubled polished 3-inch wafer but with a thickness of 500  $\mu\text{m}$ .

All the wafers are cleaned with first a  $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$  bath for 10 min and rinsing 10 min. Then a second bath of  $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$  for 10 min is done with also 10 min of rinsing. Afterwards, they are put 15 sec in a solution of 2% of HF and rinsing for 5min. Finally, the wafers are put 10 min in water with  $\text{N}_2$  bubbles before being dried. The quartz wafer skipped the HF part.

As for the nickel oxide, the parameter studied is its thickness. Based on [21], [22], it was chosen to deposit 5, 10 and 15nm of oxide to study the impact on the different metrics. It corresponds to 3min30, 7min and 10min30 of deposition time according to the recipe developed below.

For the tungsten oxide, the thickness is kept constant but the annealing temperature is different. Based on [23], [24], 4 different temperatures were chosen: 0, 200, 432 and 800°C.

Concerning the annealing, it is present at the end of for all the different processes. The classic is done for 30min at 432°C in  $\text{N}_2/\text{H}_2$  atmosphere. It is to ensure good ohmic contact and remove the dangling bonds (see Section 2.2). It also changes the crystallinity of the oxide, especially for the  $\text{WO}_3$  since the temperature will be higher.

### 3.1.4 NiO samples

The AJA sputtering equipment was used to deposit the nickel oxide for all the different samples presented in this work.



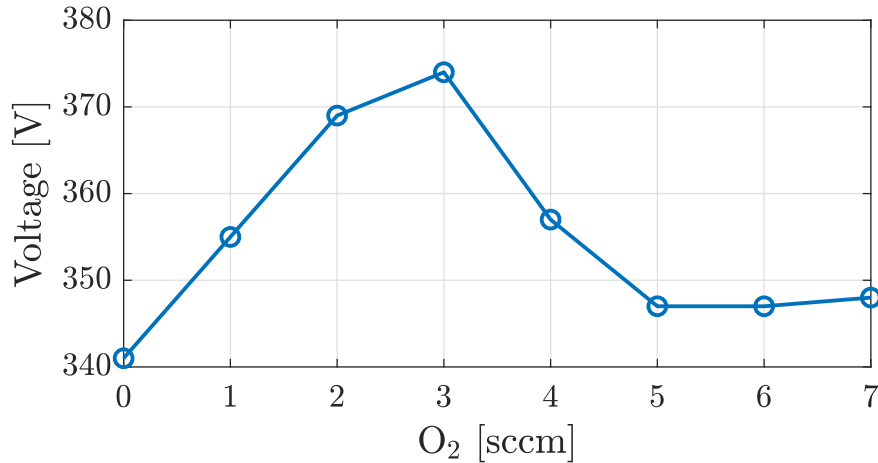
**Figure 3.5:** Photo of the AJA present in Winfab.

## Reactive gas flow and deposition rate

As said in the previous section, the  $O_2$  flow rate must be set to have an oxide deposition. A dummy wafer is placed in the equipment to determine it, and the deposition is started after a cleaning of the target (the shutter is closed and the plasma is on 5 minutes without  $O_2$  and 3 minutes with to clean the target). Four different parameters play a role in the process:

- Pressure inside the chamber
- Plasma power
- Argon flow rate
- Oxygen flow rate

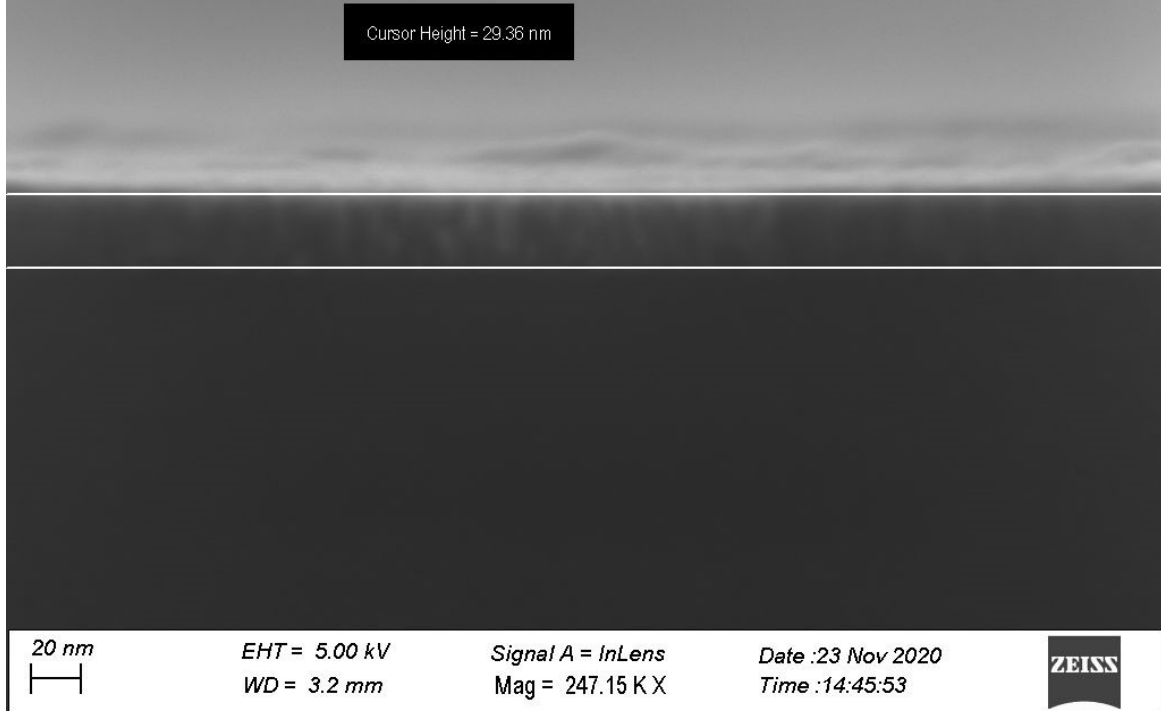
The pressure inside the chamber, the power of the plasma and the sum of the two flow rates is kept constant at 2 mTorr, 50 W and 25 sccm, respectively. The deposition starts at 25 sccm of argon and 0 sccm of oxygen. Every 3 minutes, the voltage is recorded, the flow rate of oxygen is raised by one, and argon's rate is reduced by one. Based on the result presented in Figure 3.6, 4 sccm of oxygen is chosen to deposit the nickel oxide.



**Figure 3.6:** Voltage versus the flow of oxygen for the deposition of nickel oxide.

Once the different parameters have been fixed (pressure: 2 mTorr, power: 50 W,  $O_2$ : 4 sccm and Ar: 21 sccm), the deposition rate must be determined. To do so, an other wafer is put in the AJA with a small Teflon tape on it and NiO is deposited for 20 minutes.

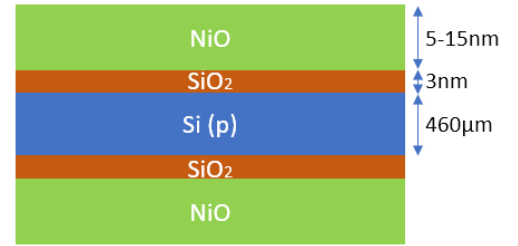
When it is finished, the tape is removed and the thickness is measured by profilometry with the Veeco Dektak 150 and ellipsometry with the Sentech SE850. For the first one, it measures the height difference and this is why the tape is needed. By removing the Teflon, the device can measure from the silicon and thus the deposited thickness. As for the second one, it measures the change of polarization of light with a spectral range from 190 nm to 900 nm. Then, the thickness is estimated by fitting an analytical model depending on the stack of material. The profilometer gave 24 nm and the ellipsometer 29nm. To settle between the two, an SEM observation was done (see Figure 3.7). It confirms the measure of 29nm, giving a deposition rate of  $\approx 1.5\text{nm/min}$ .



**Figure 3.7:** SEM image of the wafer slice. The bottom dark is silicon and the grey between the two white lines is nickel oxide.

### Lifetime measurements

Table 4 and Figure 3.8 present the process and the layout for the carrier lifetime measurement. First, standard cleaning is performed. Then, the wafers are loaded in the Koyo furnace to thermally grow 3nm of  $\text{SiO}_2$ . Afterwards, the samples are stocked at a temperature of  $110^\circ\text{C}$  in an inert atmosphere to protect the oxide while they go one by one in the AJA to deposit the nickel oxide. A fourth wafer with no deposition is made to investigate the impact of the deposition.



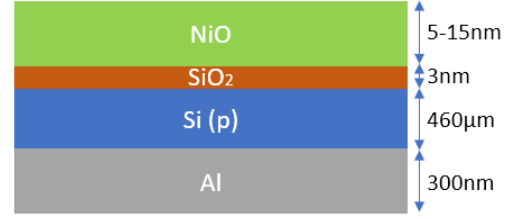
**Figure 3.8:** Layout for the lifetime measurements.

| Process                     | C1  | C2   | C3   | Si |
|-----------------------------|-----|------|------|----|
| Cleaning                    |     |      |      |    |
| Thermal oxide (3nm)         |     |      |      |    |
| NiO deposition (front side) | 5nm | 10nm | 15nm |    |
| NiO deposition (back side)  | 5nm | 10nm | 15nm |    |
| LF Measurements             |     |      |      |    |
| Annealing                   |     |      |      |    |

**Table 4:** Summary of the process for the carrier lifetime measurements for NiO. LF stands for lifetime and the black cases are to indicate an undone step.

## Electrical measurements

Table 5 and Figure 3.9 present the process and the layout for the electrical measurements. The beginning is the same as the one before. First, a standard cleaning, then the silicon oxide thermally grew and the deposition of nickel oxide on the front site. A protective resin is applied to the NiO to remove the silicon oxide at the back of the wafer. Afterwards, the wafer is plunged in BHF 50% for a period of 10sec. This will remove the SiO<sub>2</sub>. Next, the wafer is loaded in the VST (presented in Section 3.1.5) to deposit the 300nm of aluminium by evaporation. Finally, the protective resin is removed.



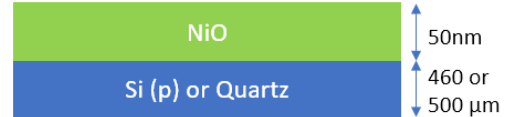
**Figure 3.9:** Layout for the electrical measurements.

| Process                     | C4  | C5   | C6   |
|-----------------------------|-----|------|------|
| Cleaning                    |     |      |      |
| Thermal oxide (2nm)         |     |      |      |
| NiO deposition (front side) | 5nm | 10nm | 15nm |
| Remove back oxide           |     |      |      |
| Al deposition               |     |      |      |
| Annealing                   |     |      |      |

**Table 5:** Summary of the process for the electrical measurements for NiO.

## Intrinsic measurements

Table 6 and Figure 3.10 present the process and the layout for the intrinsic properties measurements. For the different measurements, two types of wafers were needed: quartz and silicon. First of all, standard cleaning is performed. For the wafer in quartz, the HF part is skipped. Then, 50nm of NiO is deposited.



**Figure 3.10:** Layout for the intrinsic properties measurements.

| Process                      | M1  | M2      | M4  | M5      |
|------------------------------|-----|---------|-----|---------|
| Cleaning                     |     |         |     |         |
| Deposition 50nm (front side) | NiO | NiO     | NiO |         |
| Break in half                |     |         |     |         |
| Annealing                    |     | Classic |     | Classic |

**Table 6:** Summary of the process for the intrinsic properties measurements of NiO. The black cases are to indicate an undone step.

## Metallic layer oxidation (MLO)

For reasons that will be explained later (see Section 4.2.1), an other way of depositing nickel oxide is experimented. It still uses the AJA but the deposition is decoupled from the oxidation. First, 3nm of nickel is deposited, still by DC sputtering but with an atmosphere of nitrogen only. Then, the plasma is cut and the oxygen valve is opened for 20min to oxidise the thin layer of nickel. The process can be repeated to obtain the desired thickness. In this work, only one cycle is performed and it is then measured by XPS to determine its composition (see Section 4.1.1). This process was first tried by a former UCL doctoral student, Raphael Poulain [25].

### 3.1.5 WO<sub>3</sub> samples

For the deposition of tungsten oxide, the VST is used. It can do DC sputtering, E-beam deposition and hold multiple wafer thanks to a planetary rotation system. The first one is used to deposit the oxide, while the other is used to deposit the aluminium used as back contact for the electrical measurements.

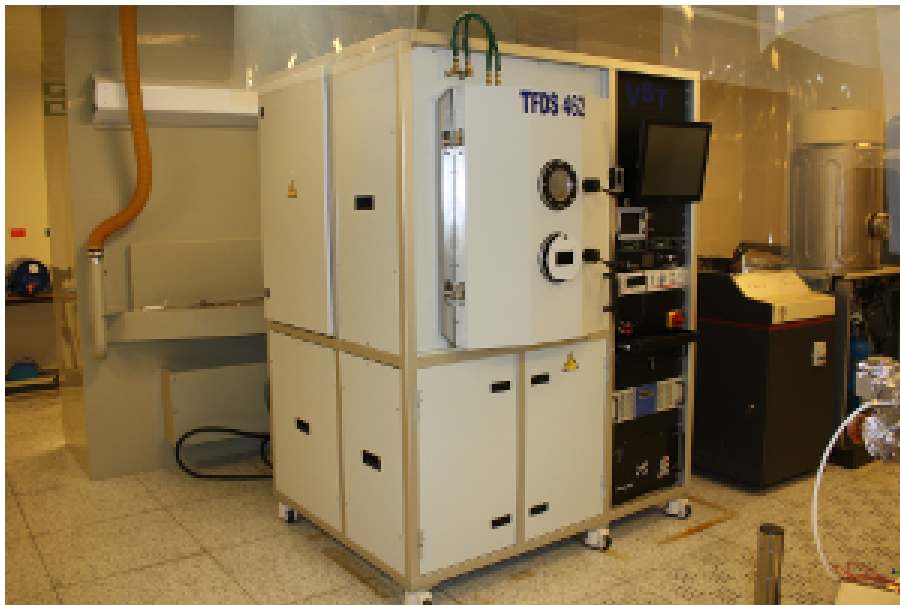
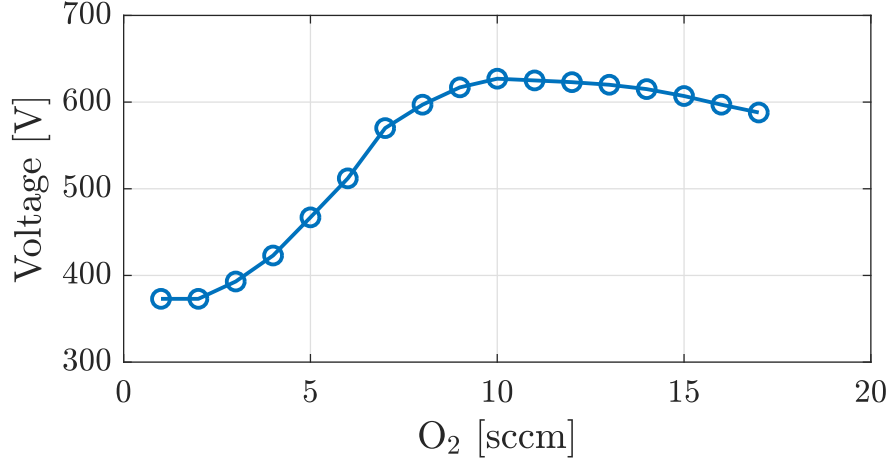


Figure 3.11: Photo of the VST present in Winfab.

### Reactive gas flow and deposition rate

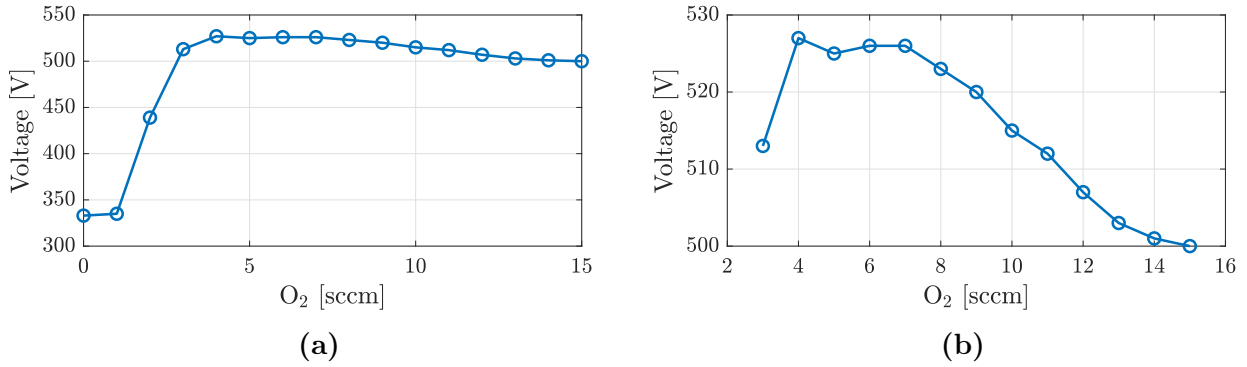
The same procedure described in Section 3.1.4 is used to determine the working flow of oxygen for the deposition of tungsten oxide but some parameters are different.

The pressure inside the chamber is 10 mTorr and the power for the plasma is set at 300W. Based on Figure 3.12 (and although the trend is the opposite of what is expected, see Figure 3.4), the oxygen flow taken is 6 sccm. However, the deposition rate is too high: after only 20min, the oxide had a thickness of 430nm. Since the target is in the order of the nanometer, the power is decreased to 100 W and the search of the working oxygen flow was redone.



**Figure 3.12:** Voltage versus the flow of oxygen for the deposition of tungsten oxide.

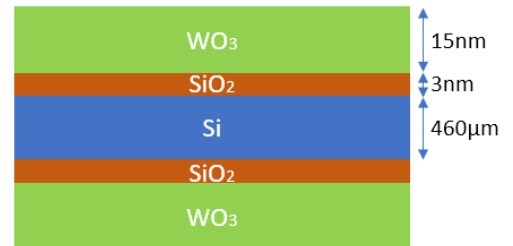
Figure 3.13 present the result at 100W. Given the trend, 2 different flows of oxygen were tested: 5 and 10 sccm. The first one gives a deposition rate of 5.6 nm/min, while the other is 2.5 nm/min. To have better precision, the last flow is chosen.



**Figure 3.13:** Voltage versus the flow of oxygen for the deposition of tungsten oxide. (a) is the whole trend and (b) is zoomed.

### Process - Lifetime measurements

Table 7 and Figure 3.14 present the process and the layout for the carrier lifetime measurement. It is nearly the same as the nickel oxide except the thickness is constant (15nm) and the annealing is done at different temperatures: 0, 200, 432 (named classic) and 800°C.



**Figure 3.14:** Layout for the lifetime measurements.

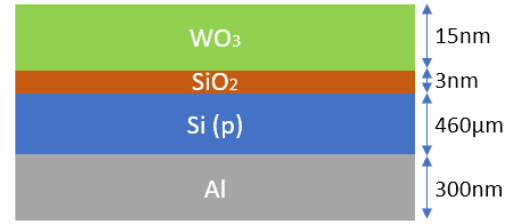


| Processes                   | LW1 | LW2 | LW3     | LW4 |
|-----------------------------|-----|-----|---------|-----|
| Cleaning                    |     |     |         |     |
| Thermal oxide (2nm)         |     |     |         |     |
| WO3 déposition (front side) | 15  |     | 15      |     |
| WO3 déposition (back side)  | 15  |     | 15      |     |
| LF Measurement              |     |     |         |     |
| Break in half               |     |     |         |     |
| Annealing                   |     | 200 | classic | 800 |
| LF Measurement              |     |     |         |     |

**Table 7:** Summary of the process for the carrier lifetime measurements for WO<sub>3</sub>. LF stand for lifetime and the black case is to indicate an undone step.

### Process - Electrical measurements

Table 8 and Figure 3.15 present the process and the layout for the electrical measurements. There are more steps for this process because it is not possible to anneal at 800°C with aluminium due to its low melting point (660°C). Instead, a first annealing is done at 800°C under a nitrogen atmosphere. There is no hydrogen just because it is not available in this furnace. Then, the silicon oxide at the back is removed by the process described earlier and the back contact is deposited. Finally, a classic annealing is performed to ensure good electrical contact.



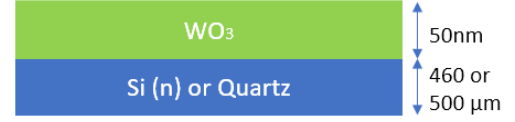
**Figure 3.15:** Layout for the electrical measurements.

| Processes                   | eW5 | eW6 | eW7     | eW8     | Si      |
|-----------------------------|-----|-----|---------|---------|---------|
| Cleaning                    |     |     |         |         |         |
| Thermal oxide (2nm)         |     |     |         |         |         |
| WO3 déposition (front side) | 15  |     | 15      |         |         |
| WO3 déposition (back side)  |     |     |         |         |         |
| LF Measurement              |     |     |         |         |         |
| Break in half               |     |     |         |         |         |
| Remove back oxide           |     |     |         |         |         |
| Al deposition               |     |     |         |         |         |
| Break in half               |     |     |         |         |         |
| Annealing                   |     | 200 | classic | 800     | classic |
| Remove back oxide           |     |     |         |         |         |
| Al deposition               |     |     |         |         |         |
| Annealing                   |     |     |         | classic |         |

**Table 8:** Summary of the process for the electrical measurements for WO<sub>3</sub>. LF stand for lifetime and the black cases are to indicate an undone step.

## Process - Intrinsic measurements

Table 9 and Figure 3.16 present the process and the layout for the intrinsic properties measurement. In this case, it is an n-type silicon wafer that is used because of a measurement technique. It needs to have the same type of conductivity as the deposited oxide: n-type [26].



**Figure 3.16:** Layout for the intrinsic properties measurements.

| Processes                    | Qwartz |     |         |     | Silicon (N type) |     |         |     |
|------------------------------|--------|-----|---------|-----|------------------|-----|---------|-----|
|                              | M3     | M4  | M5      | M6  | M9               | M10 | M11     | M12 |
| Cleaning                     |        |     |         |     |                  |     |         |     |
| déposition 50nm (front side) | WO3    | WO3 | WO3     | WO3 | WO3              |     | WO3     |     |
| Break in half                |        |     |         |     |                  |     |         |     |
| Annealing                    |        | 200 | classic | 800 |                  | 200 | classic | 800 |

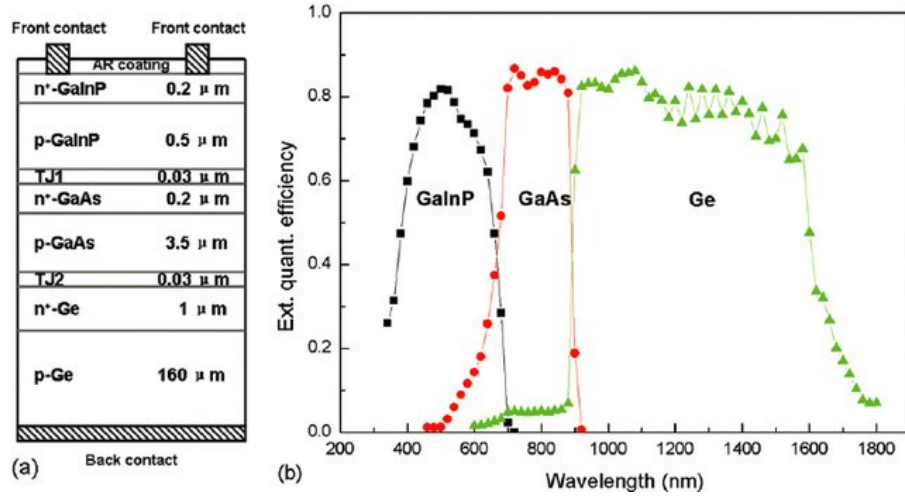
**Table 9:** Summary of the process for the intrinsic properties measurements for  $\text{WO}_3$ . LF stand for lifetime and the black cases are to indicate an undone step.

## 3.2 PV Cell overview

In a second part of the project, 3 different solar cells were irradiated using protons: triple-junction GaAs based, silicon and CIGS. They are quickly presented in this chapter.

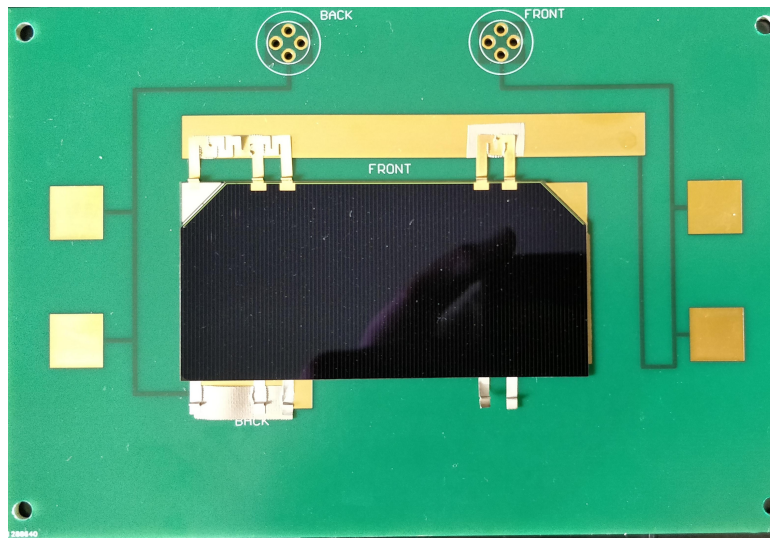
### 3.2.1 Triple-junction solar cell

As indicated by his name, a triple-junctions solar cell is 3 cells stack on each other to improve its efficiency (up to 33%). Each will absorb a specific spectral range and transmit the rest to the subsequent layers be absorbed by the one below it (see Figure 3.17).



**Figure 3.17:** (a) Schematic structure of GaInP/GaAs/Ge triple-junctions solar cell. (b) quantum efficiency of the non-irradiated sample. From [27].

In this work, the one taken is announced to have an average efficiency of 29.6% measured with the AMO spectrum, a  $V_{oc}$  of 2.69 V and an  $I_{sc}$  of 519 mA. At Welcome's laboratory under the AM1.5 spectrum, the measured characteristics were 24.6%, 2.64 V and 360 mA, respectively. Figure 3.18 shows the measured cell that was placed on a PCB to allow better handling to measure it.



**Figure 3.18:** Photo of the triple-junction solar cell on a PCB.

### 3.2.2 Silicon solar cell

To compare the more "exotic" cell, a silicon cell is also analyzed. It is the most common. Unfortunately, there is no datasheet for this one, but under the AM1.5 spectrum, the efficiency was 16.3%, 0.66V for the  $V_{oc}$  and 0.83 for the  $I_{sc}$ . Figure 3.19 shows the measured cell that was placed on a PCB to allow better handling to measure it.

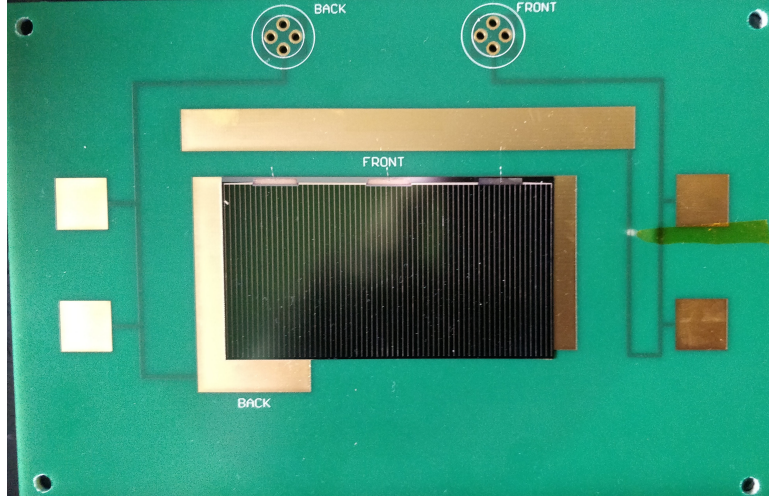


Figure 3.19: Photo of the silicon solar cell on a PCB.

### 3.2.3 CIGS solar cell

The last type of solar cell analyzed is an experimental one from UCLouvain. It is a thin-film solar cell made of copper indium gallium selenide. The one used in this thesis are made by Solliance on a glass substrate. The thickness of the absorption layer is 534nm with 23.4% of copper, 16.4% of indium, 8.2% of gallium and 52.0% of selenide. The schematic is shown in Figure 3.20.a while Figure 3.20.b shows a photo of the device. It is made up of multiple solar cells (4 grid of 8x4 are usable). But regrettably, the set-up to measure the efficiency,  $V_{oc}$  and  $I_{sc}$  is too noisy to measure such small cells.

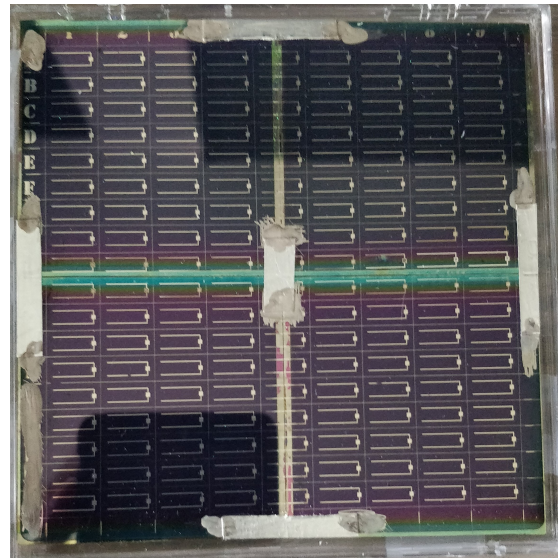
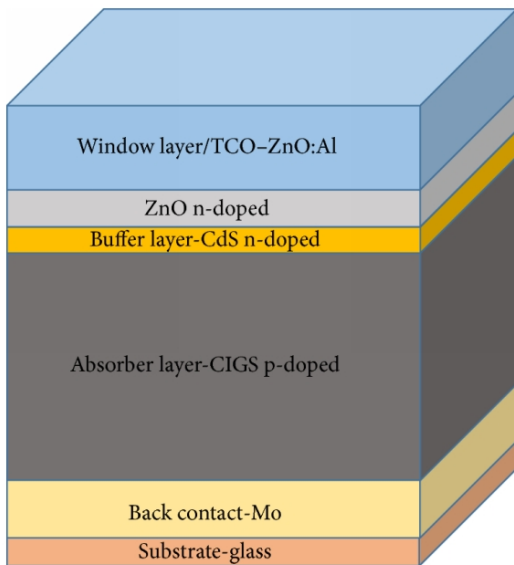


Figure 3.20: Schematic structure of a CIGS solar cell (From [28]) and photo of the cells.

### 3.3 Methods

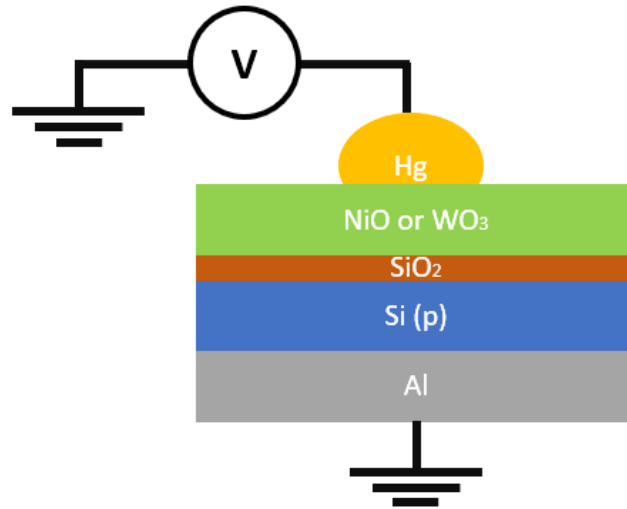
In this work, a lot of different techniques were used to analyze the different samples or devices. Nearly all methods were used to characterize the hole selective layer except the light IV and the noise measurements. As for the different solar cells, only the first four are done.

#### 3.3.1 Capacitance-Voltage

##### Tools setup

For the study of different oxides as hole selective layer, the HP484A LCR meter and a mercury probe station as a temporary contact were used. A schematic of the connection can be seen in Figure 3.21 with the mercury which act as a metal electrode with a diameter of  $907\ \mu\text{m}$ .

Three different sets of measures are performed using this probe. The first one is used to see its overall behaviour and is performed at a frequency range of 1kHz to 1Mhz and a voltage range of -5 to 5V with 51 data points. The second was used to extract the interface trap density with frequency from 1 to 10Khz and a voltage range of -3 to 1V with 101 points. The last one is for the investigation of the capacitance hysteresis. It is done at 1 and 10kHz from -3V to 1V, then from 1V to -3V with 202 data points.



**Figure 3.21:** Schematic of the electrical contact using the mercury probe.

For the different solar cells, the CV measures are performed on a shielded low signal PM8PS probe station with a four-wire configuration at a controlled temperature of  $25^{\circ}\text{C}$  for better accuracy and measurement reliability. The frequencies used are 1, 4, 7, 10 and 100Khz with a voltage range from -1 to 1.

All the measurements are conducted in the dark to prevent any parasitic illumination. There is also a delay time of 8 sec between each frequency and a hold time of 2 sec between each measurement. The amplitude of the AC small-signal applied is always 30mV.

##### Capacitance accuracy

The instrument has multiple measurements mode. In this thesis, the parallel one is used. It discriminates the output voltage as a parallel capacitance and conductance. If the last one is too large, the capacitance will be incorrectly estimated.

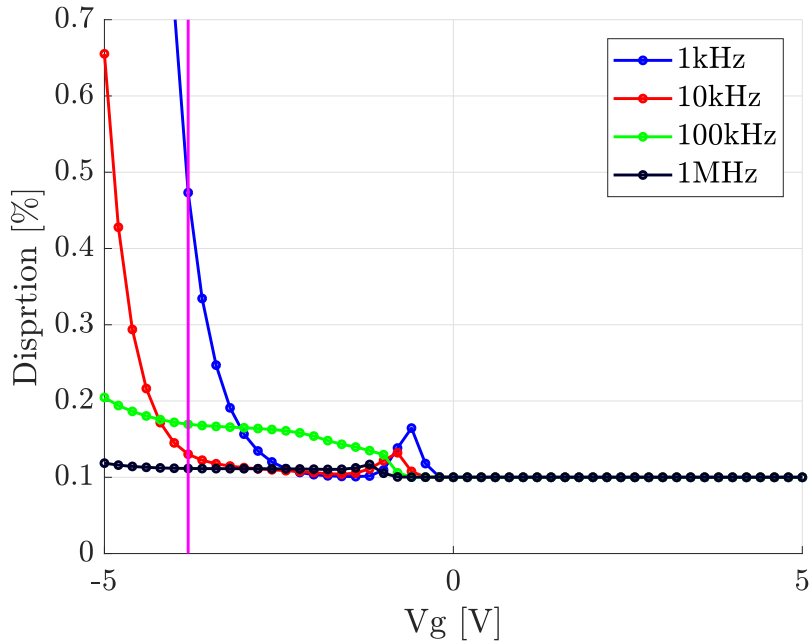
The estimate of the error is defined by:

$$error[\%] = 0.1\sqrt{1 + D^2} \quad (1)$$

Where D is the dissipation factor ( $G_p$  is the parallel conductance and  $C_p$  the parallel capacitance):

$$D = \frac{G_p}{\omega C_p} \quad (2)$$

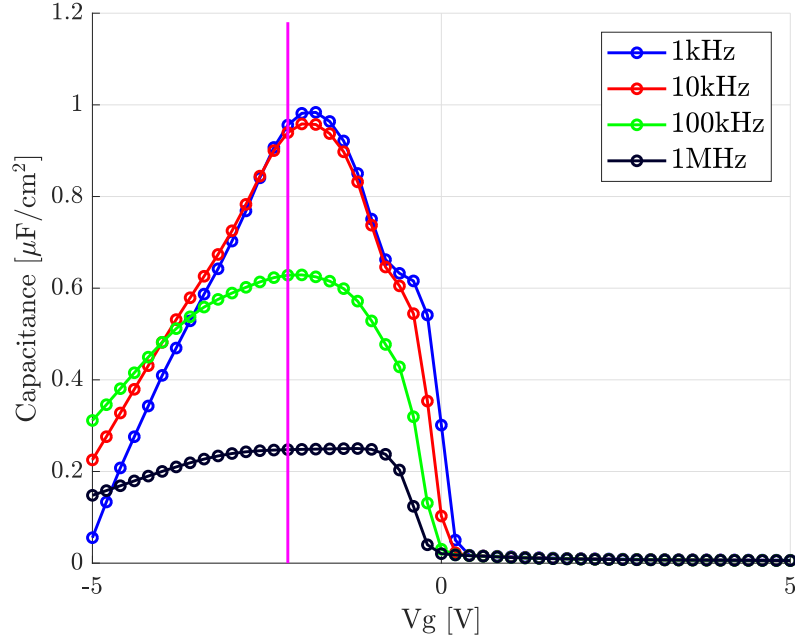
By convention, if the error is above 0.5%, the interpretation of the CV curves needs to be carefully interpreted: a tendency can be an instrument error. The limit will always be displayed on the different CV graphs. If not, all the points have a dispersion below 0.5%.



**Figure 3.22:** Dispersion factor versus the voltage for stack of Al/Si/SiO<sub>2</sub> 3nm. The pink line is the limit when  $D > 0.5\%$

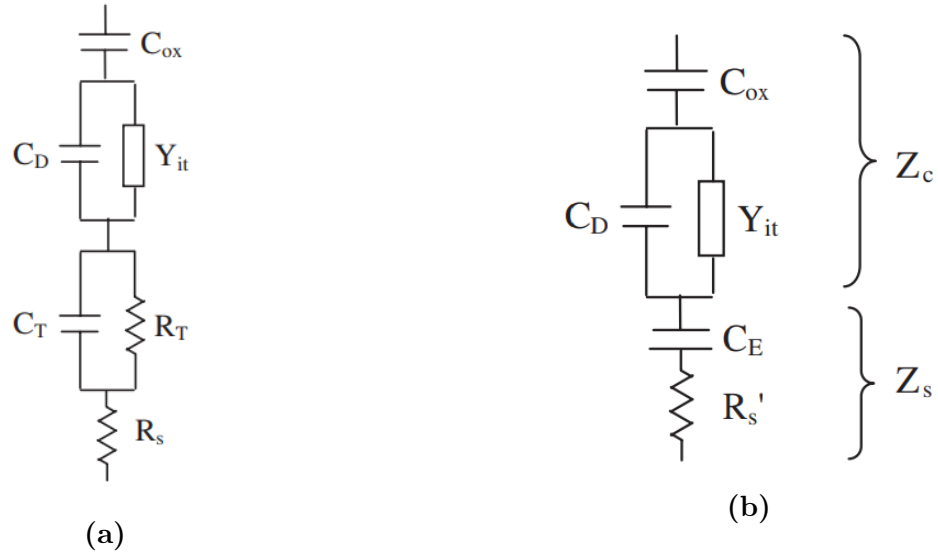
### Capacitance correction

Figure 3.23 presents the CV measurement for a stack of Al/Si/SiO<sub>2</sub>/NiO. The maximum capacitance in the accumulation region is supposed to be constant but due to a parasitic series resistance or high traps densities [29], it decreases with the frequency.



**Figure 3.23:** Capacitance versus the voltage stack of Al/Si/SiO<sub>2</sub>/NiO. On the left of the pink line, the dispersion is greater than 0.5%.

In order to remove its influence, the six-element circuit model from [30] is used. It decomposed the stack of material into 6 different components presented in Figure 3.24.  $C_{ox}$  is the intrinsic oxide capacitance,  $C_D$  the depletion layer capacitance,  $Y_{it}$  the interface trap charge admittance,  $R_T$  and  $C_T$  are the resistance and capacitance of the SiO<sub>2</sub> layer and  $R_S$  is the series resistance.



**Figure 3.24:** Presentation of the electrical six-element circuit model (a) and the model used for the calculation (b). The development to go from (a) to (b) can be found in [30].

The corrected capacitance ( $C_c$ ) and conductance ( $G_c$ ) are:

$$C_c = \frac{(w^2 C_m C_E - G_m^2 - w^2 C_m^2) (G_m^2 + w^2 C_m^2) (C_E)}{(w^2 C_E^2) [G_m (1 - R'_S G_m) - w^2 R'_S C_m^2]^2 + (G_m^2 + w^2 C_m^2 - w^2 C_m C_E)^2} \quad (3)$$



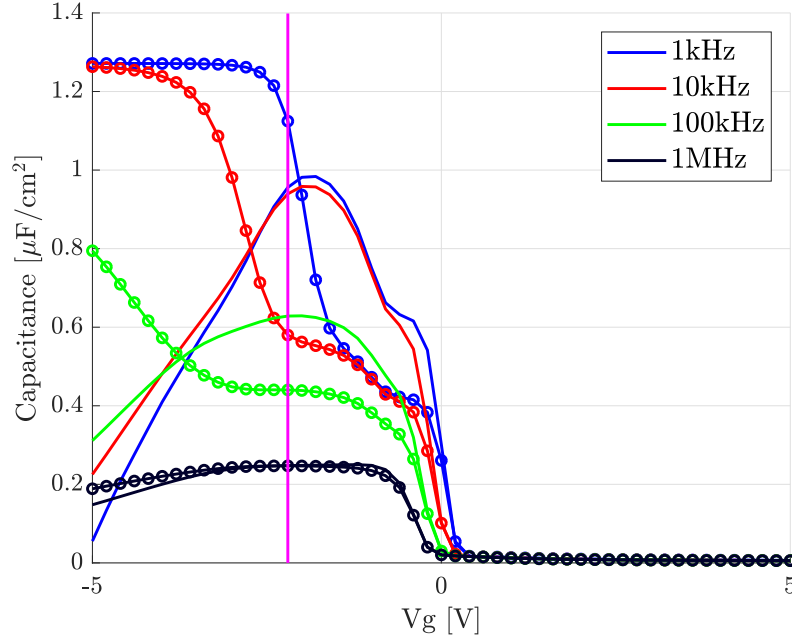
$$G_c = \frac{[G_m (1 - R'_S G_m) - w^2 R'_S C_m^2] (G_m^2 + w^2 C_m^2) (w^2 C_E^2)}{(w^2 C_E^2) [G_m (1 - R'_S G_m) - w^2 R'_S C_m^2]^2 + (G_m^2 + w^2 C_m^2 - w^2 C_m C_E)^2} \quad (4)$$

With  $C_m$  and  $G_m$  the measured capacitance and conductance in parallel,  $C_{ma}$  and  $G_{ma}$  the maximum measured capacitance and conductance and  $w$  the angular frequency.  $C_E$  and  $R'_S$  expressions are defined below:

$$C_E = \frac{-C_{ox} (G_{ma}^2 + w^2 C_{ma}^2)}{w^2 (C_{ma}^2 - C_{ma} C_{ox}) + G_{ma}^2} \quad (5)$$

$$R'_S = \frac{G_{ma}}{G_{ma}^2 + w^2 C_{ma}^2} \quad (6)$$

The complete development can be found in, [30] and the results of the correction is shown in Figure 3.25. The correction is not perfect, but it brings the first 3 curves together.



**Figure 3.25:** Capacitance versus the voltage stack of Al/Si/SiO<sub>2</sub>/NiO with the correction in the marked line and the measured with the normal one. On the left of the pink line, the dispersion is greater than 0.5%.

For the solar cell, it is different. The parallel conductance and capacitance are transformed into series:

$$R_s = \frac{G_p}{G_p^2 + w^2 C_p^2}$$

$$C_s = \frac{G_p^2 + w^2 C_p^2}{w^2 C_p}$$



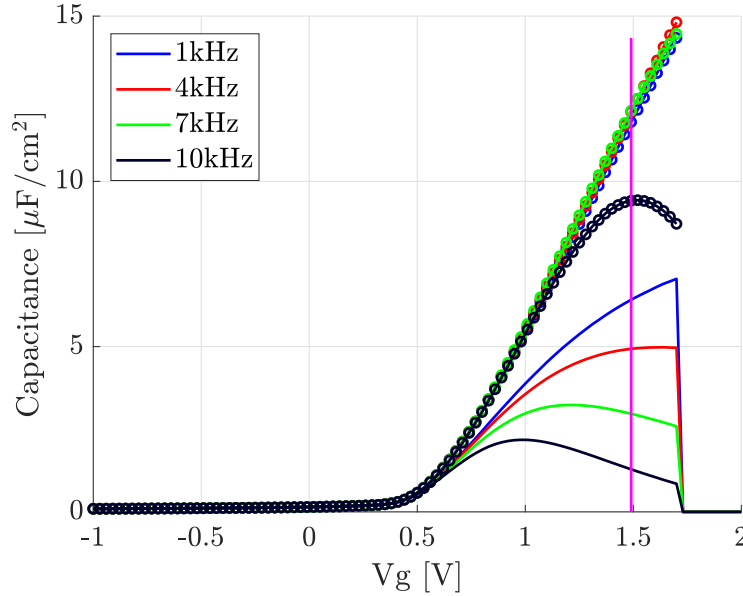
Then, the parasitic series resistance ( $r_s$ ) is estimated graphically by try and error until the capacitance is independent of frequency and it transformed again in parallel conductance:

$$R_{s,corrected} = R_s - r_s$$

$$G_{p,corrected} = \frac{C_s}{1 + (w R_{s,corrected} C_s)^2}$$

$$C_p = \frac{1}{R_{s,corrected} + (w^2 R_{s,corrected} C_s^2)^{-1}}$$

Figure 3.26 presents the correction. It works well except at the end for the 10kHz. But it is when the dispersion is greater than 0.5%. Therefore, it can be a wrong estimation of the capacitance. The 100Khz is not shown, but it will be discussed in the Results section.



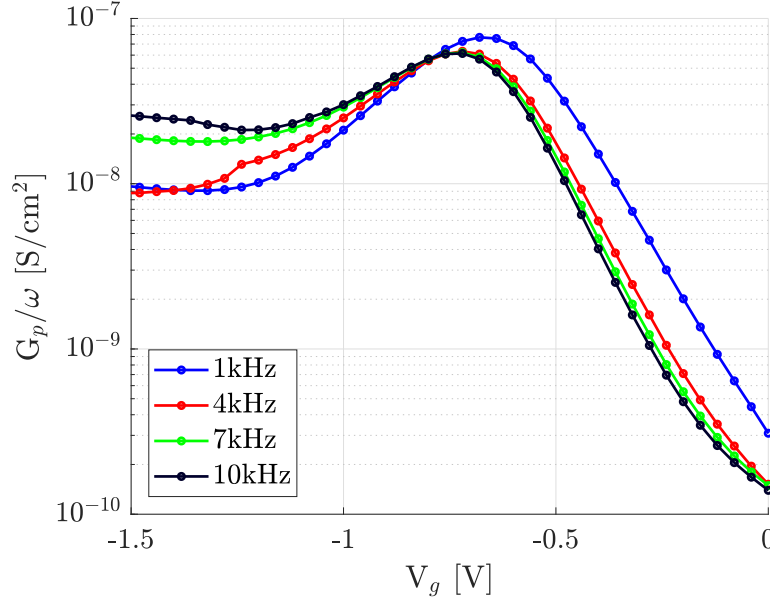
**Figure 3.26:** Capacitance versus the voltage of the silicon solar cell with the correction in the marked line and the measured with the normal one. On the right of the pink line, the dispersion is greater than 0.5%.

### $D_{it}$ extraction

To extract the density of interface traps ( $D_{it}$ ) of the NiO and  $WO_3$  stacks, the conductance technique was used. It is the most accurate interface state extraction procedure within the range of  $8 \cdot 10^9 - 5 \cdot 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$  [31], but it is dependent on the series resistance. When an AC signal is applied around the Fermi level, majority carriers are captured or emitted, changing occupancy of interface trap levels in a small energy gap centred around the Fermi level ( $E_F$ ). This will translate to a rise in the parallel conductance around  $V_{fb}$ .

When plotting  $G_p/w$  versus the voltage (see Figure 3.27), the height of the peak give direct information about  $D_{it}$  (with  $A$  the measurement area,  $q$  the charge of an electron,  $G_p$  the parallel conductance and  $w$  the angular frequency):

$$D_{it} \approx \frac{2.5}{qA} \left( \frac{G_p}{w} \right)_{\max} \quad (7)$$

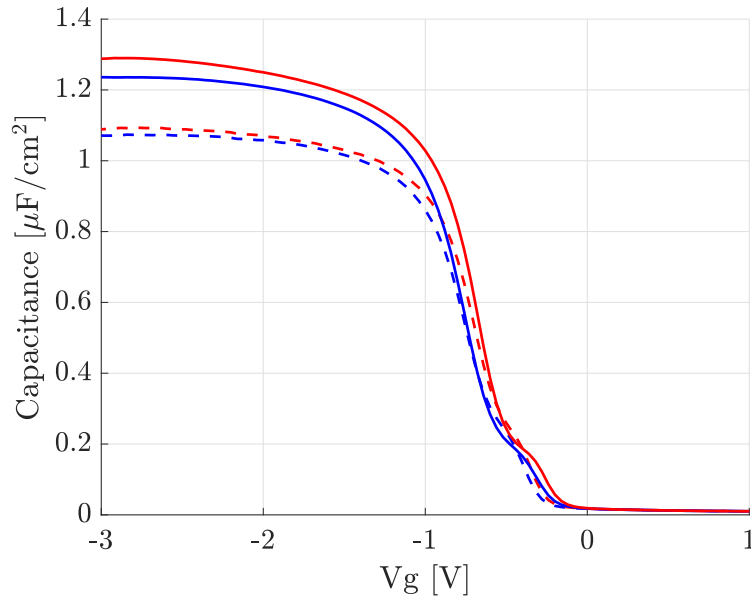


**Figure 3.27:**  $\frac{G_p}{\omega}$  versus the applied voltage for the Al/Si/SiO<sub>2</sub> stack.

Thus, according to Equation (7) and Figure 3.27, the interface traps density of the Al/Si/SiO<sub>2</sub> stack is  $1.2 \cdot 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ .

### Mobile charge

An other piece of information that can be extracted from the CV measurement are the mobile charge. When a negative to positive to negative signal is applied, the capacitance shows an hysteresis due to mobile charge present in the oxide:



**Figure 3.28:** CV hysteresis measurements of SiO<sub>2</sub> 3nm. The solid lines represent the measure at 1kHz and the dashed at 10kHz. The red indicates a measure negative to positive and the blue the opposite, positive to negative.

The link between the change of the flatband voltage is given by:

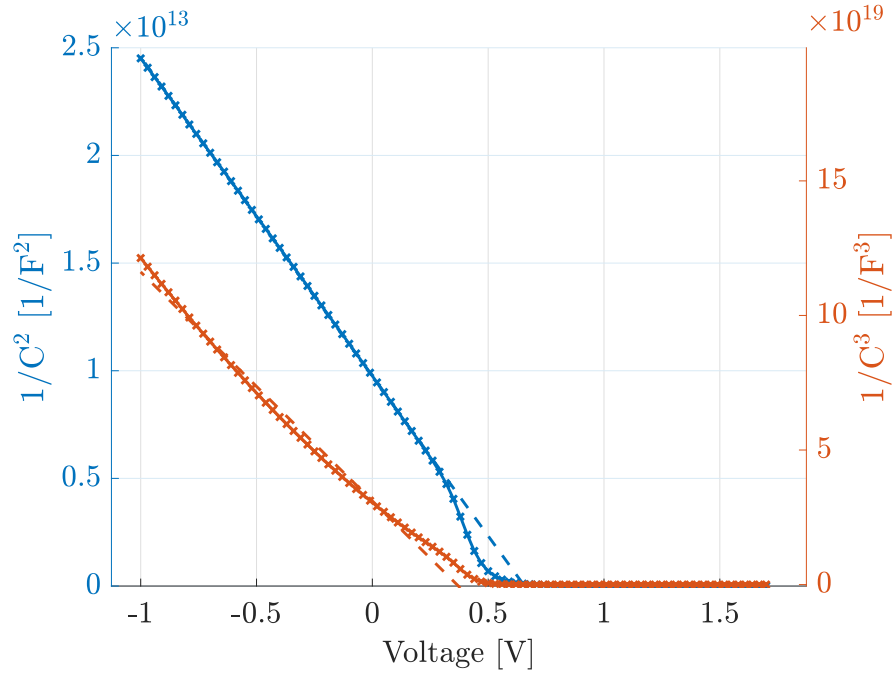
$$N_t = C_{ox} \times \frac{\Delta V_{fb}}{q} \quad (8)$$

Where  $N_t$  is the mobile charge concentration in  $\text{cm}^{-3}$ ,  $C_{ox}$  is the oxide capacitance in  $\text{F}/\text{cm}^2$ ,  $\Delta V_{fb}$  is the change of flatband voltage and  $q$  is the elementary charge.

### Apparent doping extraction

For a PN junction like a solar cell, the apparent doping versus depth can be deduced from CV measurements [32]. However, this technique cannot make the difference between the real doping profile and the defects. So it can be used to approximate the penetration depth of the radiation by comparing before and after the radiations [33].

In order to do this measurements, the  $1/C^2$  and  $1/C^3$  versus the voltage is plotted. The one with the best linearity is used in Equation (9) and it allows to determine if the doping is uniform or with a gradient [34]. The built-in voltage is also extracted and will set the limit where the formula is correct.



**Figure 3.29:** Plot of  $1/C^2$  and  $1/C^3$  versus the voltage for a silicon solar cell. The dashed lines are the linear regression.

Since the linearity is better with  $1/C^2$  ( $R^2 \approx 1$ ), the doping can be considered uniform and the junction has a built-in voltage of 0.66V.

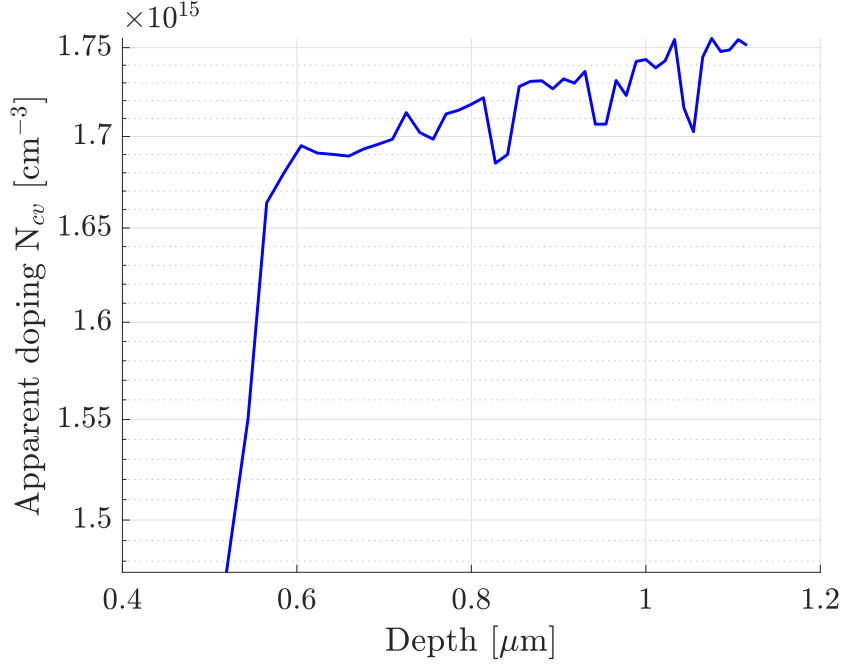
Then, the apparent doping concentration is estimated with:

$$N(w) = \frac{2}{q\epsilon_0\epsilon_r A^2 \left[ d(1/C^2)/dV \right]} \quad (9)$$

With  $q$  the electric charge,  $A$  the area of measure,  $\epsilon_0$  the vacuum permittivity,  $\epsilon_r$  the relative permittivity. If the linearity would have been better with the  $1/C^3$ , it would have replaced

the  $1/C^2$  in the formula. The depth ( $w$ ) is calculated from the formula of the thickness of a dielectric:

$$w = \frac{\varepsilon_r \varepsilon_0 A}{C(V)}$$



**Figure 3.30:** Apparent doping concentration versus the depth for the silicon solar cell.

### 3.3.2 Dark IV

#### Tools setup

The dark current versus the voltage measurements used the same setup as the capacitance-voltage measurement.

#### The two-diode model

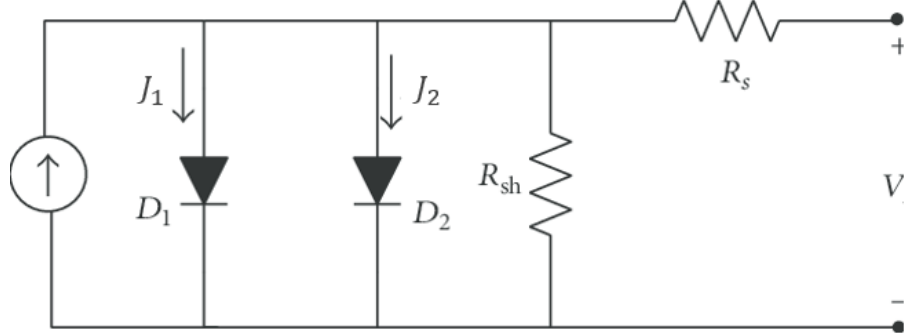
The analytical two-diode model of a PV-cell in the dark is used to extract the electrical parameters of the different devices. The latter allows to evaluate the radiation degradation. Equation (10) present the various parameters with  $J(V)$  being the current density:

$$J(V) = \underbrace{J_1 \left[ \exp \left( \frac{q(V + R_s J)}{n_1 k T} \right) - 1 \right]}_1 + \underbrace{J_2 \left[ \exp \left( \frac{q(V + R_s J)}{n_2 k T} \right) - 1 \right]}_2 - \underbrace{\frac{V + R_s J}{R_{shunt}}}_3 \quad (10)$$

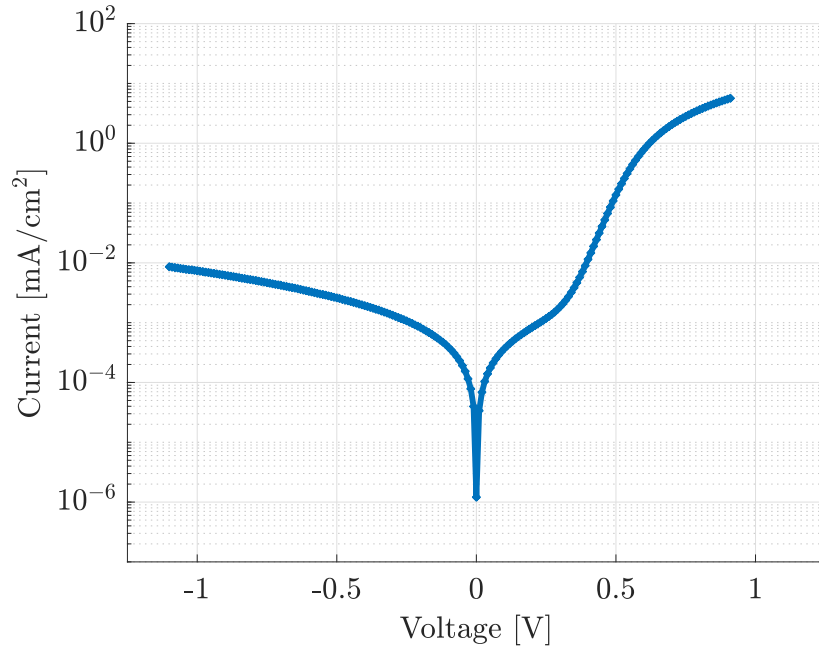
1. The first part of the equation is related to the first diode ( $J_1$  on Figure 3.31). It represents the diffusion current that dominates at high voltage. It is characterized by its current density  $J_1$  and its ideality factor  $n_1$ .
2. The second part is for the second diode that represents the losses by generation/recombination due to defect. It is characterized by its current density  $J_2$  and its ideality factor  $n_2$ . It

dominates at a low and negative voltage. The radiation is expected to create defects and thus significantly impact its parameters.

3. The last one is for the impact of the shunt and series resistances. The equivalent electrical circuit is presented in Figure 3.31. It has to be noted the difficulty to differentiate the impact of the series resistance and the second diode.

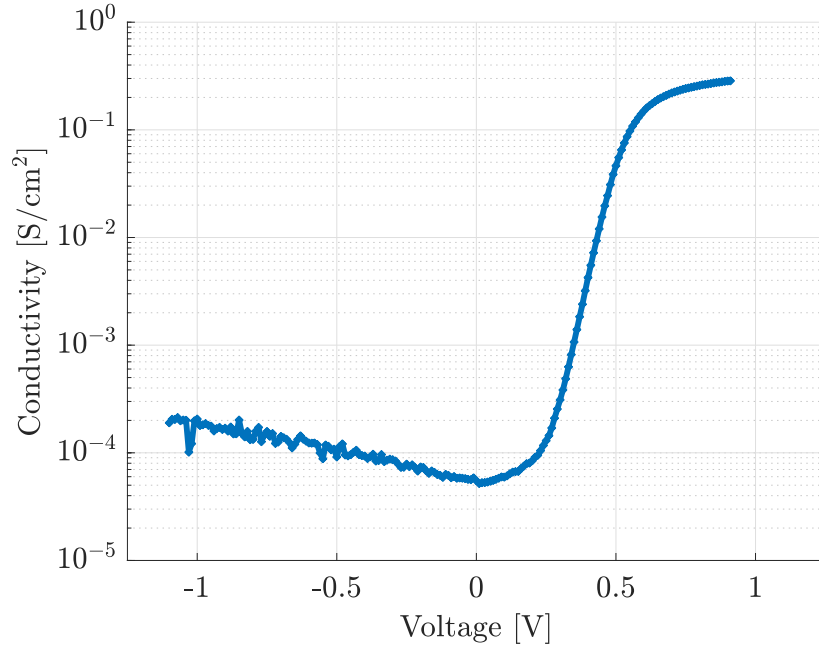


**Figure 3.31:** Equivalent electrical circuit of the 2 diodes model. Image from [35].



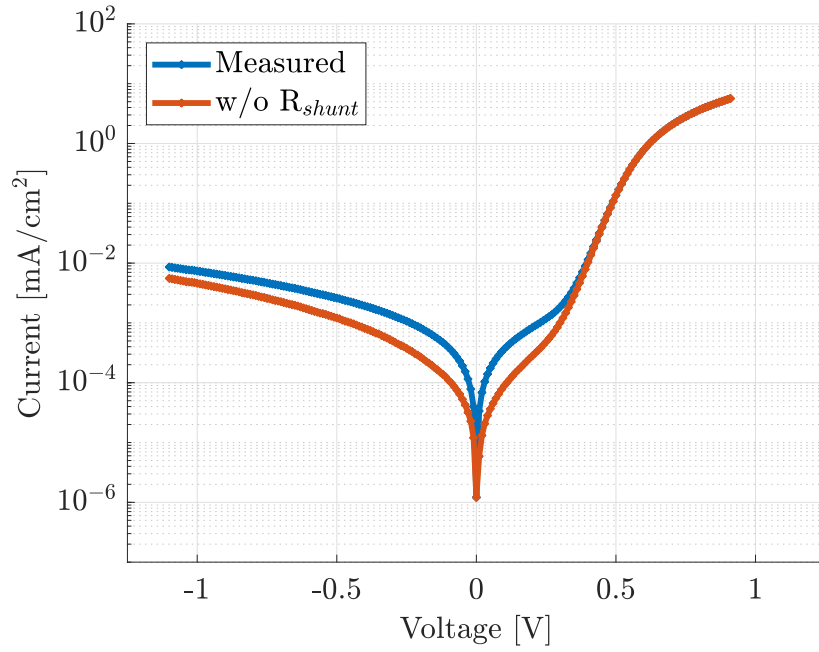
**Figure 3.32:** IV curve of a CIGS cell.

To illustrate the process to extract all these different parameters, the curve of a CIGS solar cell is taken (see Figure 3.32). The different resistances are first determined. Primarily, the current is derived by the voltage (see Figure 3.33). Then, the shunt resistance is taken as the mean of 5 points of the invert of the derivative around zero. If the series resistance has an impact, the derivative will be a plateau at high voltage. It is again taken as a mean of 5 points. If there is no plateau, the series is put at zero.



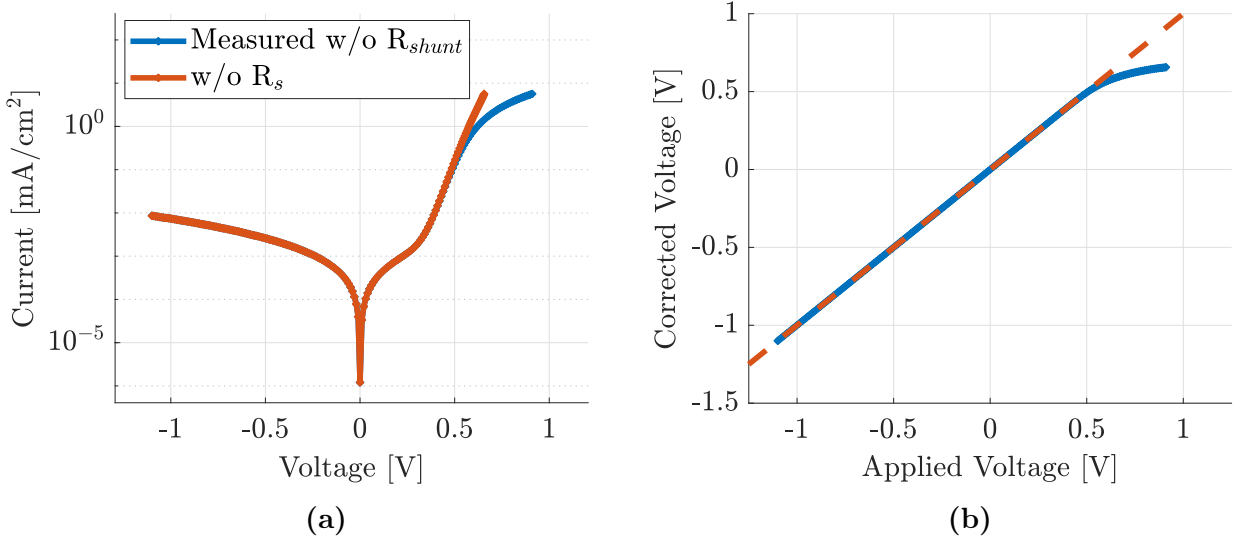
**Figure 3.33:** Example of the derivative of the current by the voltage.

Then, the current going through the shunt resistance is removed ( $J = J - V \cdot R_{shunt}$ ):



**Figure 3.34:** Comparison with and with-out (w/o) the shunt resistance.

The voltage is corrected with the series resistance ( $V = V - I/R_s$ ):



**Figure 3.35:** (a) Comparison with and with-out (w/o) the series resistance and (b) the impact of the voltage correction. The dashed lines are when  $V_{Corrected} = V_{Applied}$ .

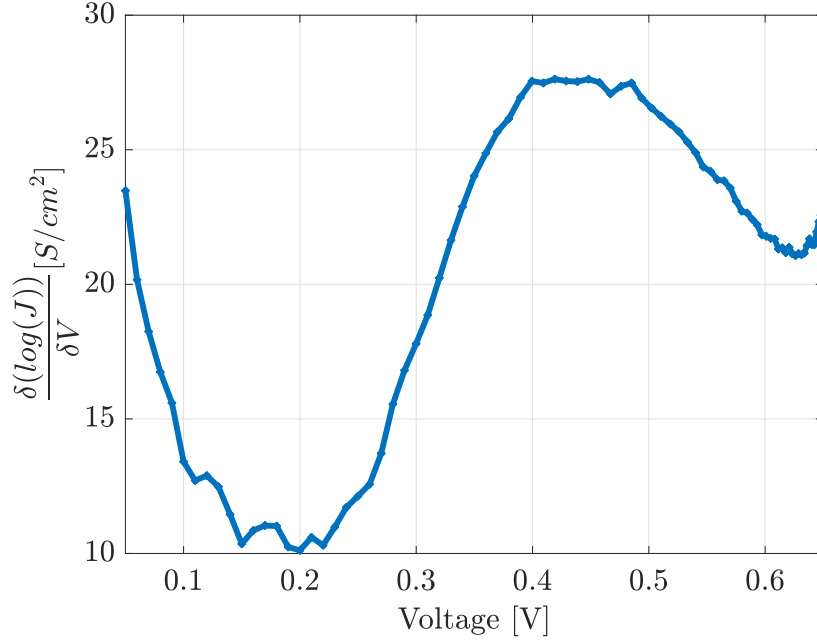
To determine the ideality factor  $n_1$  or  $n_2$ , a small mathematical development is required. To isolate them from Equation (10), a diode has to be neglected when the other is prevailing:  $D_2 \ll D_1$  at high voltage and it is the opposite at low voltage (see Figure 3.38). Equation (10) is also taken without the  $R_{shunt}$  and  $R_s$  (already removed, see Figures 3.34 and 3.35) and the minus 1 is neglected. Then, a logarithm is applied (just  $n_1$  is represented but it is the same development for  $n_2$ ) :

$$\log(J(V)) = \log(J_1) + \left( \frac{qV}{n_1 kT} \right) \quad (11)$$

Afterwards, Equation (11) is derived and is represented in Figure 3.36:

$$\frac{\delta \log(J(V))}{\delta V} = \left( \frac{q}{n_1 kT} \right) \quad (12)$$

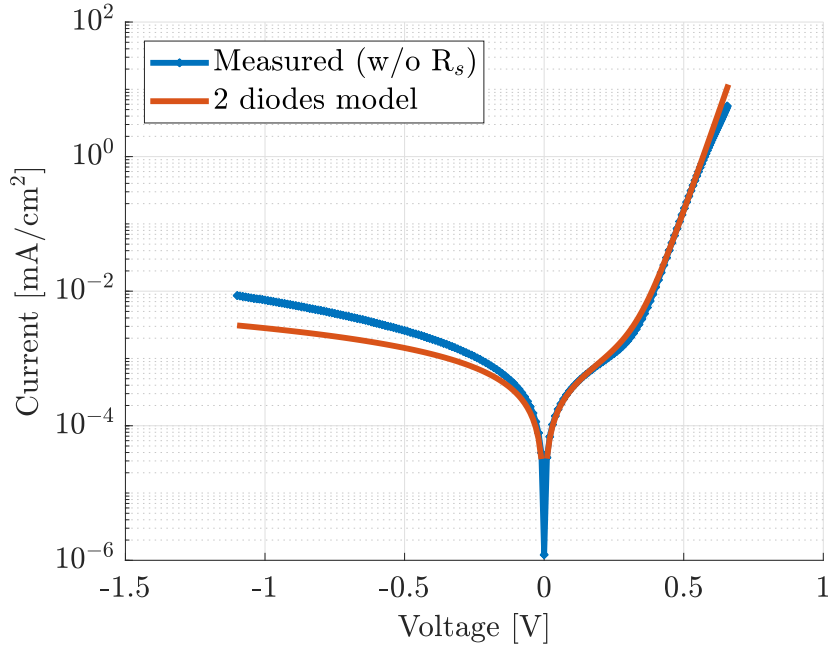




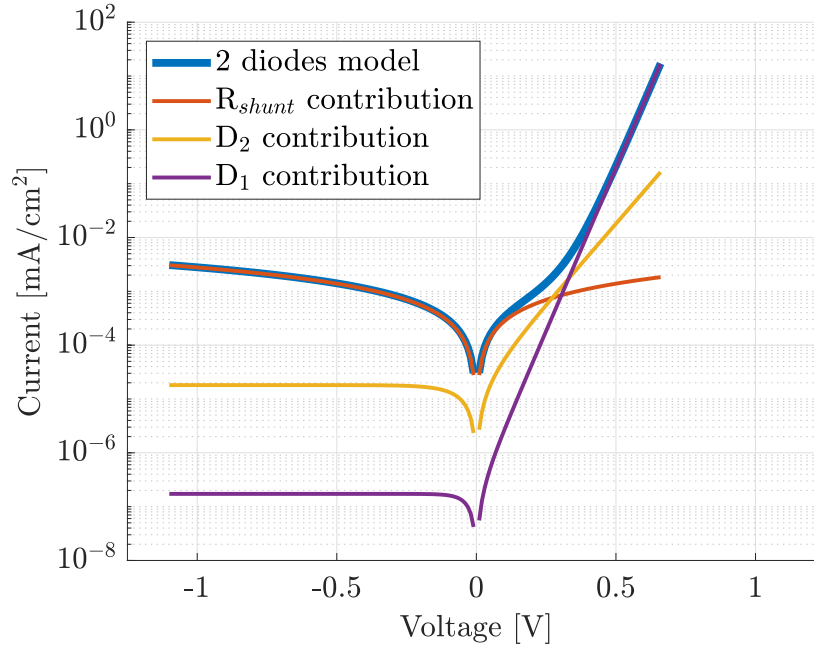
**Figure 3.36:** Derivative of  $\log(J)$  versus the voltage.

The minimum on Figure 3.36 is where  $D_2$  dominates and the maximum is where  $D_1$  dominates. The ideality factor is isolated from Equation (12). When they are calculated,  $J_2$  and  $J_1$  are estimated to correspond graphically (see Figure 3.37).

Since it is complicated to make the difference between  $R_{shunt}$  or  $J_2$ , an overestimation of one can explain the difference between the measured and the model in reverse. It can also be a loss not taken into account in the model. Finally, the different contributions can be seen in Figure 3.38.



**Figure 3.37:** Comparison between the 2 diodes model and the measurement (without the series resistance).



**Figure 3.38:** The different contributions of the 2 diodes model.

### 3.3.3 Noise

Noise measurements are only done on the PV cells. This measure contributed to study the different defects in the junction by polarising it at different levels and plotting the current spectrum density or the current versus time. Since defects are a source of noise with their own signatures, different mechanisms could be identified but it is out of scope for this thesis. Only a qualitative approach is done in this work.

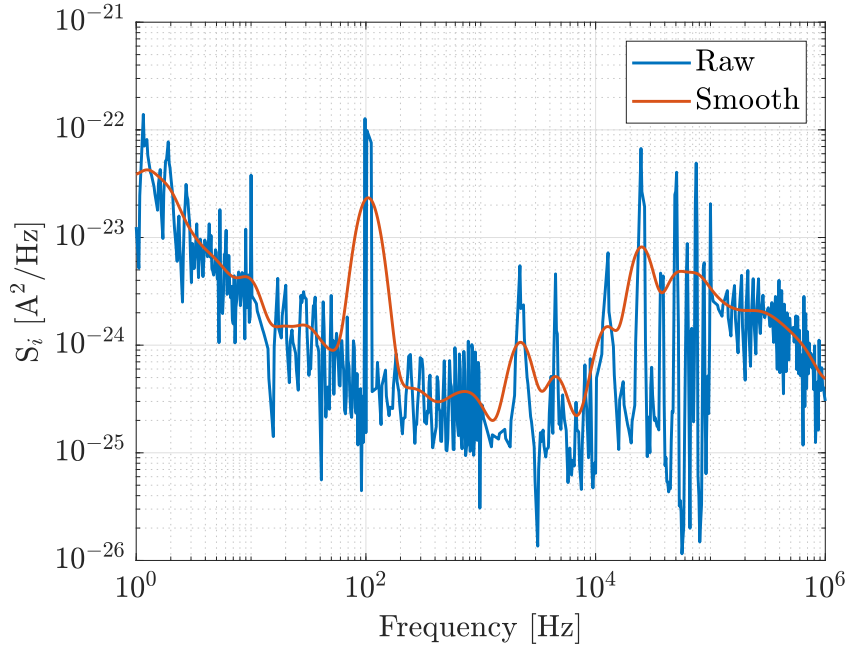
### Tools setup

The MPI TS3000-SE is used to perform the different measurements. First, an IV measure is done with 110 data points between -1 and 1 volt. It calibrates the instruments in function of the level of current.

Afterwards, 22 polarisation points are chosen to measure the noise, 10 in the negative and 12 in the positive (for the CIGS, it rises to 21), with an analysed spectrum from 1 to 1 Mhz.

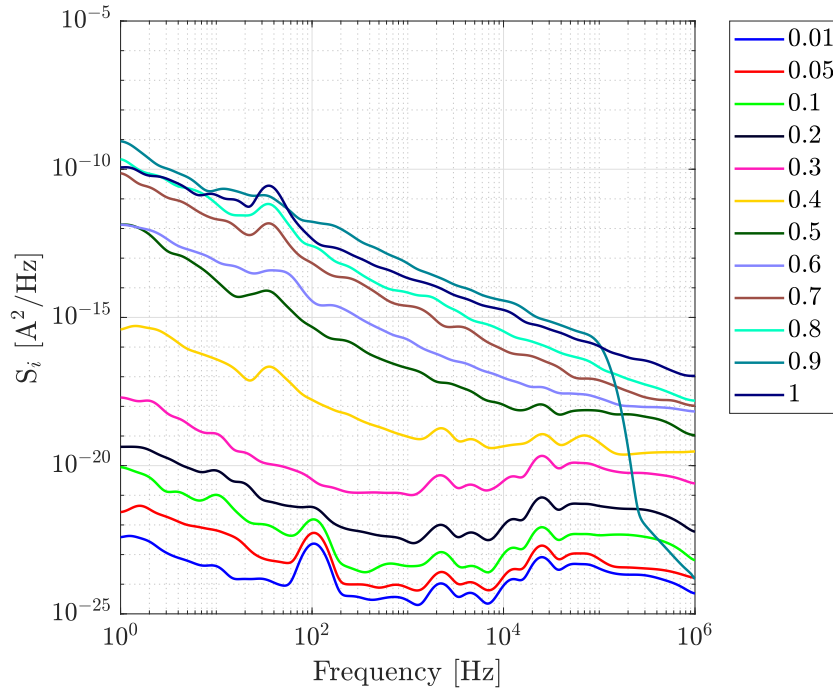
### Method

Figure 3.39 present the raw data. Since the measure is noisy, it is smoothed by a sliding average of 5 points 60 times. Only the smoothed data are represented in this thesis.



**Figure 3.39:** Raw and smooth current spectrum density for the silicon solar cell.

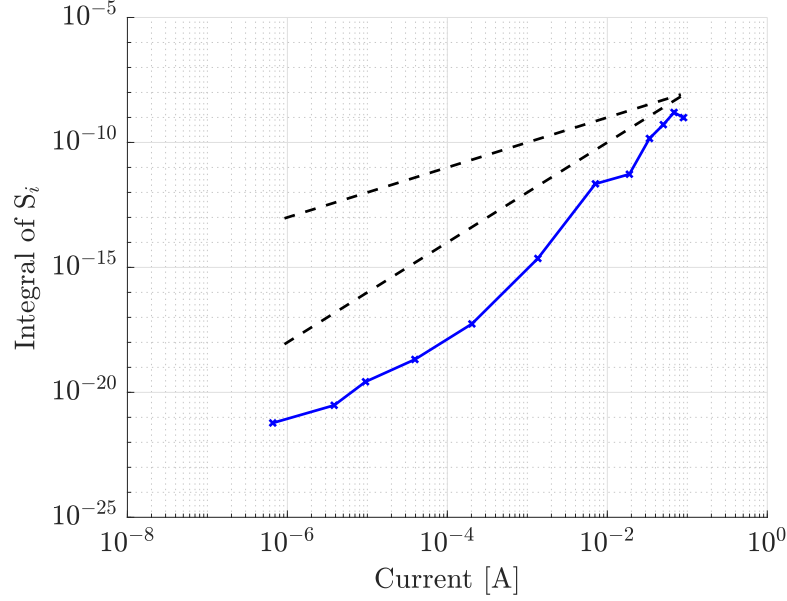
This type of measure is extremely sensitive to ambient noise. Around 100Hz and 1Khz, a contamination appears (fluctuations). It is present only on some measurements and the cause can not be determined. Therefore, only the data before 100Hz are analysed.



**Figure 3.40:** Current spectrum density for the silicon solar cell at different positive polarisation (in volt).

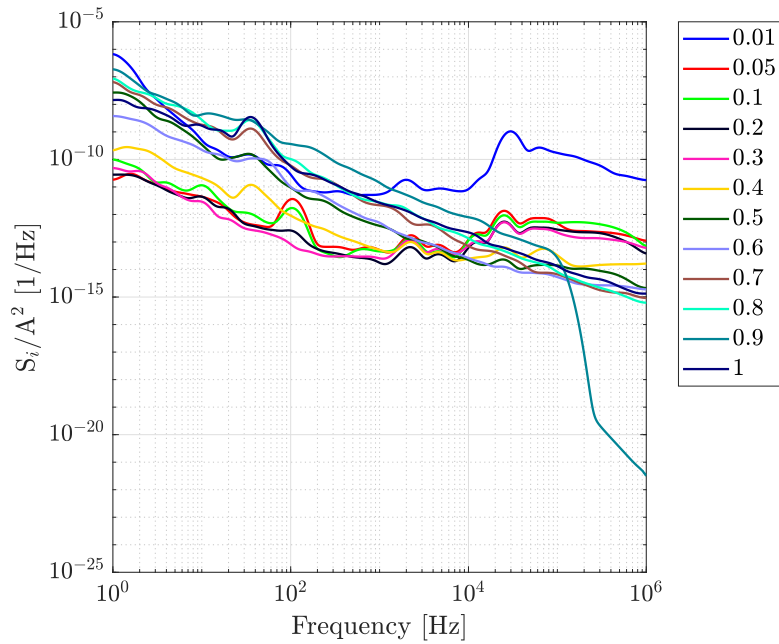
Figure 3.40 shows the different measures at different polarisations (at 1V, the noise perturbation does not seem active). It appears there is more noise at a higher voltage. However it is normal

since there is also more current. To cancel this effect, the current spectrum is divided by how the spectrum evolves with the current. To do so, the integral of the spectrum from 1 to 100 Hz versus the current is plotted in Figure 3.41. The integral also compares the effect of radiation.



**Figure 3.41:** Integral of current spectrum versus the current. The first dashed lines are when  $S_i \propto I$ , the second is when  $S_i \propto I^2$ .

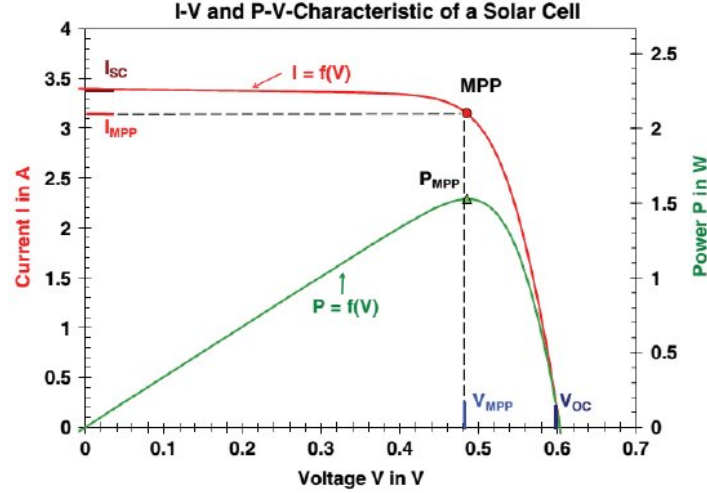
Given that the spectral density is proportional to the current squared, it is divided by this value. Figure 3.42 presents the result. At low voltage, the curves stay regrouped and have the same slope.



**Figure 3.42:** Current spectrum density divided by the current squared for the silicon solar cell at different positive polarisations (in volt).

### 3.3.4 Light IV

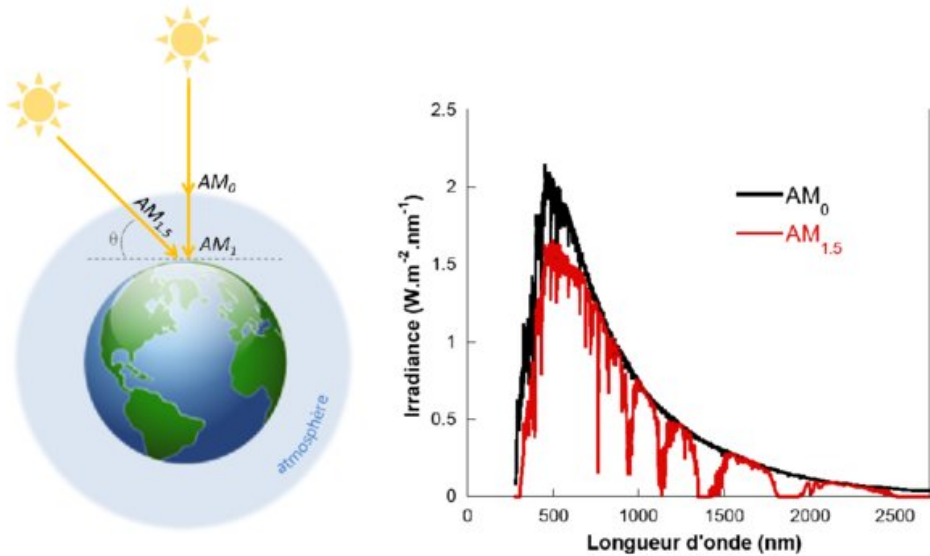
Although the dark IV measurements give several meaningful information for the different solar cells, the behaviour under light is equally important. It gives the solar energy efficiency as well as the open-circuit voltage ( $V_{oc}$ ), the short circuit current ( $I_{sc}$ ) and the fill-factor (FF). This last metric measures the quality of the solar cell by comparing the maximum power ( $V_{mpp} * I_{mpp}$ ) to the maximal theoretical power ( $V_{oc} * I_{sc}$ ).



**Figure 3.43:** Characteristic curves I-V and P-V of a solar cell. From [36].

#### Tools setup

Measuring these different characteristics is performed the Quicksun 120A. It has a calibrated lamp with a spectre AM1.5. This spectre is the benchmark of the industry for the simulation of the solar spectre at mid-altitude. This light spectrum might cause an issue for the triple-junction solar cell since they are optimised to work in space, the AM0 spectrum (discussed in Section 4.3). The different AM spectrum are presented in Figure 3.44.



**Figure 3.44:** Presentation of the different AM spectrum. From [37].

### 3.3.5 Minority carrier lifetime

As explained in Section 2.1, when a hole created from an electron-holes pair arrives at the back contact, it can be recombined with an electron because of different defects, thus lowering the efficiency. Hence the focus on the lifetime ( $\tau_{eff}$ ) to evaluate the quality of the sample: a high one means low defects and a possible higher efficiency.

#### Tools setup

To measure it, the symmetric wafer created in Section 3.1.4 and Section 3.1.5 are used. The instrument is the Sinton Instruments WCT-120 using the Quasi-Steady Photoconductance (QSPC) technique [38].

#### Surface recombination rates (SRV)

A quantity to compare result done on different wafer is the surface recombination rate (SRV) measured in cm/s. It measures the velocity at which the carrier recombine. Unless stated otherwise, it is estimated at an injection level of  $1 \cdot 10^{14} \text{ cm}^{-3}$ . Equation (13) present the mathematical expression.

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{S_{front} + S_{back}}{W} \quad (13)$$

Where  $W$  is the wafer thickness ( $460 \mu\text{m}$ ) and  $S_{front}$  and  $S_{back}$  represent the recombination occurring at the front and back sides of the wafer. Since the measured wafer is symmetrical (see Figure 3.1)  $S_{front} = S_{back}$ .  $\tau_{bulk}$  can be estimated infinite because of the use of high-quality wafer. So Equation (13) is simplified :

$$S_{eff} \leq \frac{W}{2 \tau_{eff}} \quad (14)$$

### 3.3.6 XPS

The X-ray photoelectron spectroscopy is used to confirm the deposition of nickel oxide by the classic deposition and the metal layer oxidation technique (MLO).

It is also used to measure the thickness of thermal grown and intrinsic  $\text{SiO}_2$  or the oxidation of nickel for the MLO deposition.

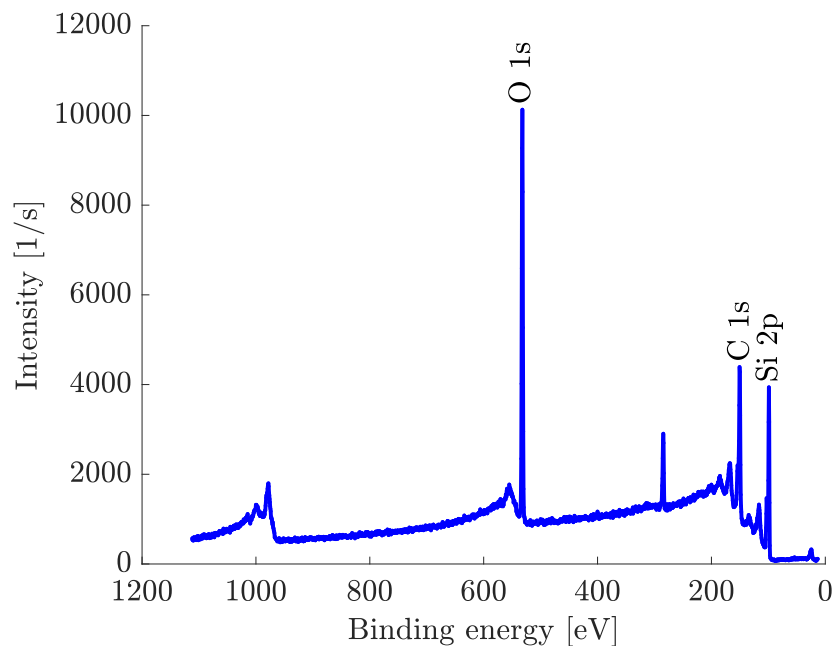
#### Tools setup

The machine used is the SSX 100/206 spectrometer from Surface Science Instruments (USA): monochromatized and micro-focused  $\text{AlK}_\alpha$  X-ray beam and is represented in Figure 3.45.



**Figure 3.45:** Photo of the XPS at UCLouvain. From [39].

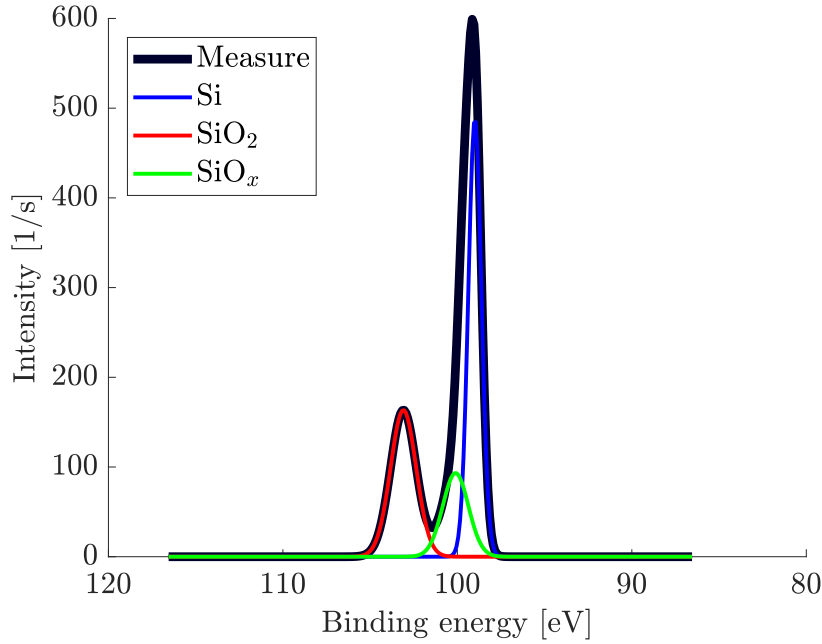
The working principle is explained on the UCLouvain site[39]: "A sample, introduced in an ultra-high vacuum chamber, is bombarded with an X-ray beam. The kinetic energy (in electron volts, eV) of emitted electrons of all elements (except H and He) present at the surface (analyzed depth between 1 and 10 nm) is measured with a precision of about 0.2 eV. The shape and position of peaks depend on the chemical state of the element (the so-called " chemical shift " effect). Area of peaks used in combination with sensitivity factors allows calculating mole fractions with a detection limit of a few tenths of percent."



**Figure 3.46:** XPS analysis of a silicon wafer.

Analysing the height of the different peaks allows to measure the height of the different layers [40]. For example, the native  $\text{SiO}_2$  of silicon wafer is measured. To do so, the silicon peak is decomposed with the contribution from Silicon,  $\text{SiO}_2$  and  $\text{SiO}_x$  minus the background (see Figure [3.47]). It is possible because when the silicon is bond with one or 2 oxygen, its maximum

position is moved. By comparing the height of the different contributions, the thickness of native  $\text{SiO}_2$  can be estimated at  $1.2(\pm 0.1)\text{nm}$ .



**Figure 3.47:** Peak of the Si 2p from Figure 3.46 zoomed with the different contribution.

### 3.3.7 XRD

X-ray diffraction analysis (XRD) is used to determine the crystallographic structure by sending an X-ray and measuring the scattering angles that leave the material.

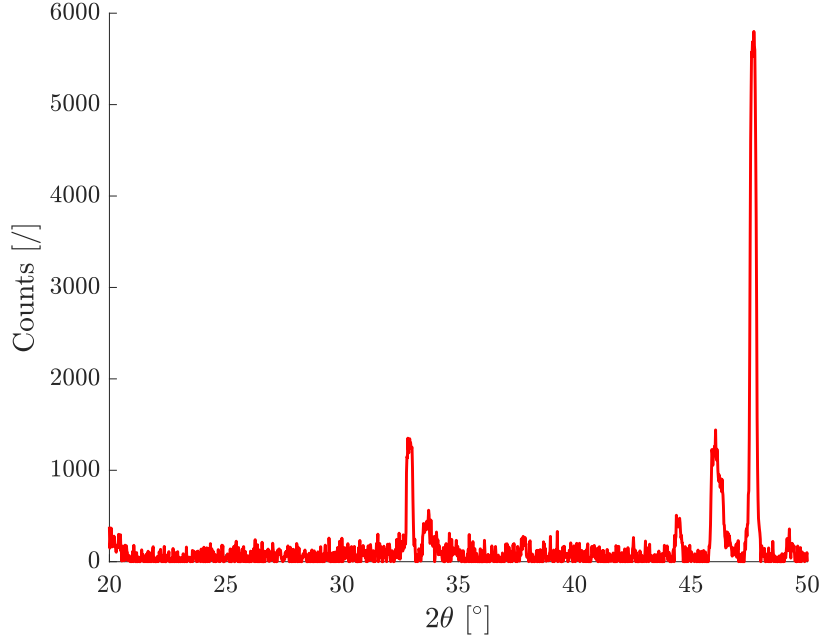
The crystallographic structure of the different samples change with the annealing. At first, it was to compare the different crystallinity of the different samples layouts (see Figure 3.1) since the thickness greatly influences it [41], especially at this scale (5 to 50nm). But regrettably a Grazing incidence XRD is required to measure thin-layer and the UCLouvain is not equipped. Thus, only the samples with 50nm of oxide are analyzed.

#### Tools setup

The system used to perform XRD measurement is set at a voltage of 45 kV and a current of 40mA with  $\text{Cu K}\alpha$  radiation ( $\lambda = 15.4 \text{ \AA}$ ). The  $2\theta$  angle started at  $15^\circ$  and ended at  $83^\circ$  with a step size of  $0.02^\circ$ . Only the area of interest, from 20 to 50 degrees, is presented.

An example of the analysis on a silicon wafer is presented in Figure 3.48.



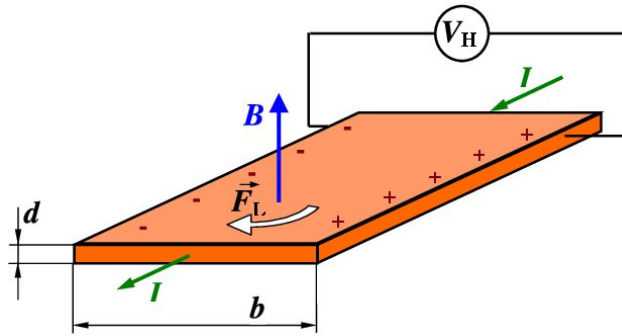


**Figure 3.48:** XRD analysis of a silicon wafer.

### 3.3.8 Hall and Van der Pauw measurements

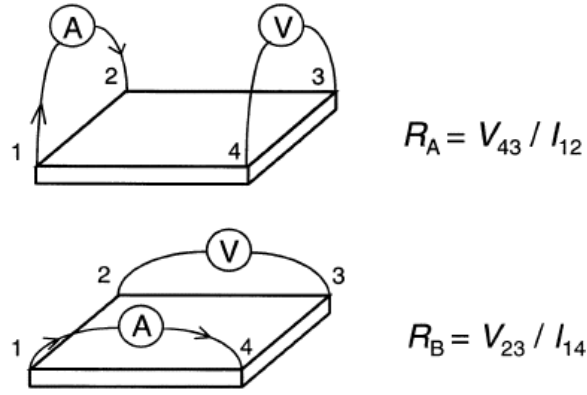
To measure the mobility (and other intrinsic properties, like the bandgap), the oxide required a certain thickness. Otherwise, the measure will quantify the interface or the substrate. So the measure is done on a 50nm oxide and the hypothesis that the properties are the same at 15nm is made. Obviously, more tests are required to confirm this hypothesis, but it is outside of the scope of this thesis.

The working principle of the Hall effect is to measure the deflection of the electrons, with the hall voltage ( $V_H$ ), when a current is applied through the sample under a perpendicular magnetic field.



**Figure 3.49:** Schematic setup for the measurement of the Hall effect. Here,  $b \approx 1\text{cm}$  and  $d=50\text{nm}$ . From [42].

Then, the Van der Pauw technique allows knowing the sheet resistivity ( $R_s$ ) by measuring two different resistivities (presented in Figure 3.50) and by respecting the relation in Equation (15).



**Figure 3.50:** Measurement of a square conductivity sample in the Van der Pauw geometry. From [\[43\]](#).

$$e^{-\pi R_a/R_s} + e^{-\pi R_b/R_s} = 1 \quad (15)$$

By knowing the sheet resistivity and the Hall voltage, the mobility is obtained with (I is the current and B the magnetic field):

$$\mu = \frac{|V_H|}{R_s I B}$$

### Tools setup

A small piece of the oxide deposited on the quartz substrate is cut in order to obtain a square of 1cmx1cm to perform this measure. Then, four-wire are placed at the 4 corners with silver paste to ensure a good electrical contact.

This setup is placed inside a small chamber where the temperature and pressure are controlled (310K and 1E-4 mTorr). Finally, this chamber is placed inside an electromagnet and the measurement can start.

Five consecutive repetitions are performed for each samples measured. For each, 4 different repetitions are made: positive/negative current and positive/negative magnetic field. The working parameters are 10 nA, 8000 G and a reading delay of 4 seconds. Figure [3.51](#) presents the setup.



**Figure 3.51:** Photo of the hall setup. The electromagnet is on the right and the different SMU and temperature controller are on the left.

### 3.3.9 UV visible

The transmission and reflection of the different samples with 50nm of oxide are measured in the UV-visible spectrum (200 to 800nm). To determine the bandgap, the tauc relation is used, which is given by

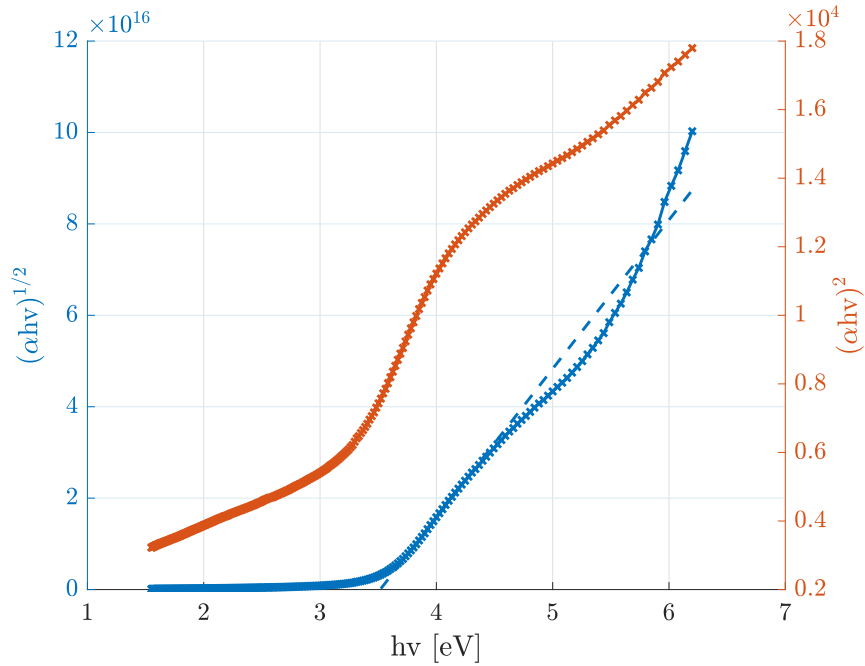
$$ahv = A(hv - E_g)^n \quad (16)$$

Where  $hv$  is the photon energy ( $hv = 1240/\text{wavelength}(\text{nm})$ ),  $E_g$  the bandgap,  $A$  a coefficient,  $n$  will depend on the electronic transition (direct or indirect) and  $a$  is the absorption coefficient:

$$a = \frac{1}{t} \ln \left[ \frac{(1 - R)^2}{T} \right] \quad (17)$$

With  $t$  the thickness (50nm),  $R$  the reflection and  $T$  the transmission.

Finally, if  $(ahv)^{\frac{1}{n}}$  versus  $hv$  is plotted, a straight line should appear with either  $n$  equals 2 or  $1/2$ . If the line is linear after being at zero with  $1/2$ , then the transition is direct, indirect if it is with  $n$  equals 2. The bandgap is the interception of the linear part when  $(ahv)^{\frac{1}{n}} = 0$ . Figure 3.52 presents the two cases with the regression to calculate the bandgap.



**Figure 3.52:** Tauc plot for  $n=2$  in blue and  $n=1/2$  in orange. The dashed lines are a linear regression of the linear part to calculate the bandgap,  $E_g=3.5$  eV in this case.

# Chapter 4

## Results

This chapter presents the different results obtained during this work. It starts with the characterisation of what has been fabricated in Winfab.

First, the composition and thickness of the silicon oxide and NiO, done by two different recipes, are studied. Unfortunately, there was not enough time to do the same analysis on the tungsten oxide.

Second, the samples created with 50nm of metal oxide (NiO and WO<sub>3</sub>) are analysed in partnership with UMons to determine their intrinsic properties (bandgap and mobility). Their crystallinity is also checked by XRD. The idea was to transpose the result to the stacks studied, which have a much smaller thickness (5-15nm). However, the XRD analysis with smaller thickness is not feasible at UCLouvain.

Thirdly, different parameters concerning the oxide on the stack are studied to assess the quality of the interfaces with the carrier lifetime and CV measurements. Concerning the role of the metals oxides as a hole-selective layer, it is investigated by IV measurements and the possible leakage mechanisms are discussed.

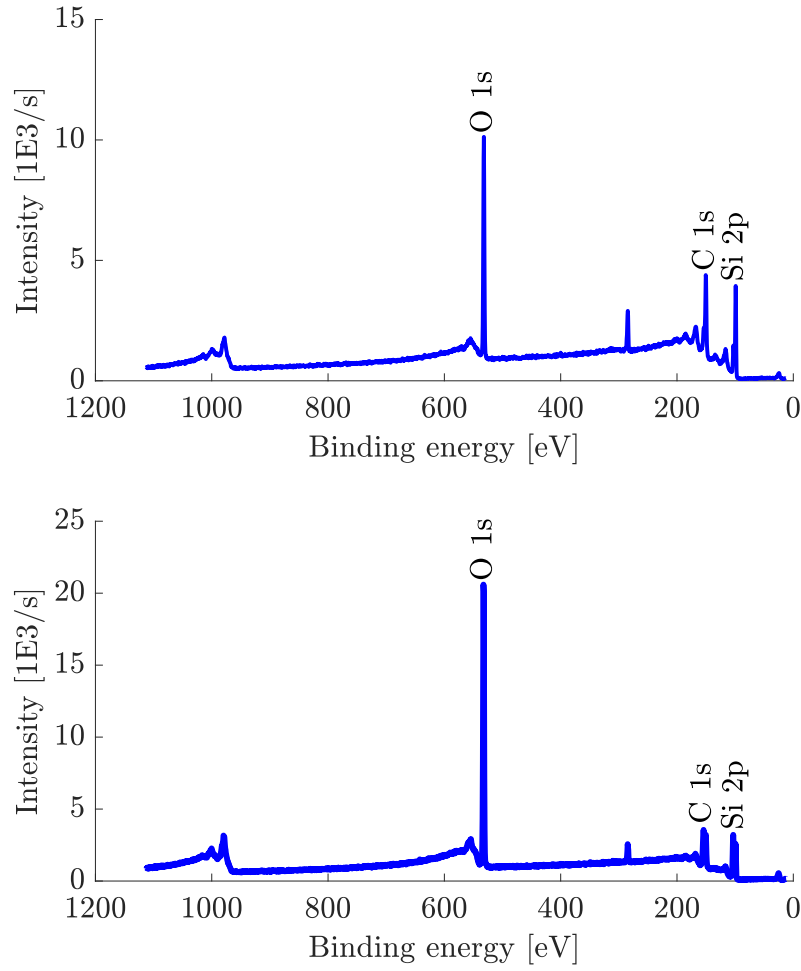
Finally, the degradation by 10 MeV protons radiations on various solar cells (triple-junction, silicon and CIGS) is investigated by dark and light IV, dark CV and noise measurements.

### 4.1 Characterisations of thin films

#### 4.1.1 Composition and thickness

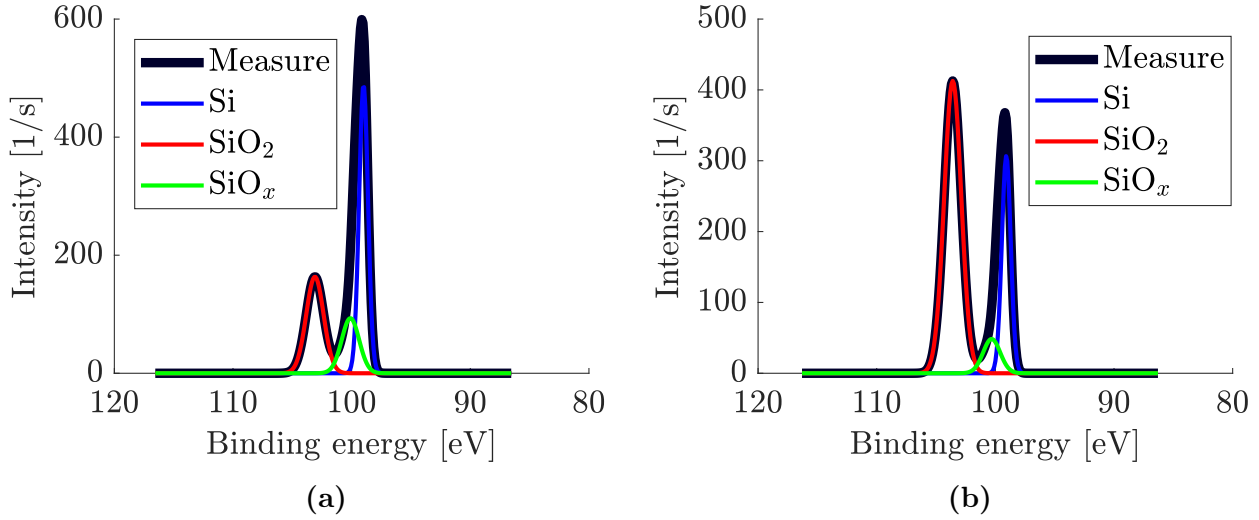
The composition of 4 different samples are analysed using the XPS: NiO, NiO by MLO, native and 3nm SiO<sub>2</sub>. The thickness of the first layers of the last three samples is extracted using the technique describes in [40] by comparing the attenuation of the second layer signal due to the first layer.

For the two silicon dioxides (showed in Figure 4.1), the calculated contributions of oxygen from the different species present (SiO<sub>x</sub>, O=C-O, C=O, O-C-O, C-O and C-(C,H)) are inferior to the one measured from the oxygen peak (O 1s). It indicates the presence of hydroxide and/or water molecules sufficiently attached to the SiO<sub>2</sub> surface to withstand a high vacuum. To keep the interface clear between the silicon oxide and the metal oxide for the rest of the process, the wafers are kept above 110°C before the different oxide deposition.



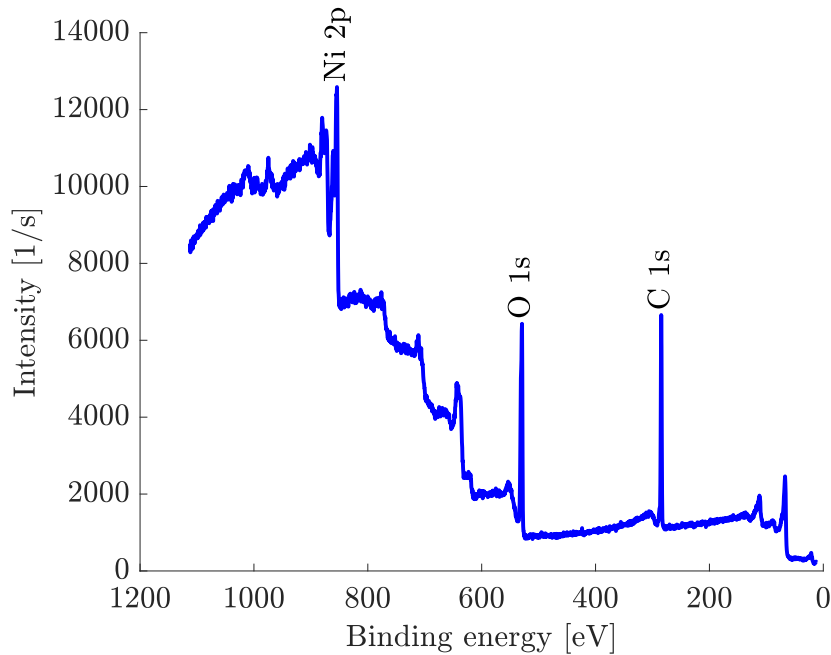
**Figure 4.1:** XPS analysis of a silicon wafer (up) and the SiO<sub>2</sub> 3nm (down).

As for the different thicknesses, the decomposition of the Si 2p peaks is shown in Figure [4.2](#). From their relative's intensity, the height of the silicon oxide is calculated. The native has a layer of  $1.2(\pm 0.1)\text{nm}$  while the other has  $2.9(\pm 0.2)\text{nm}$  of SiO<sub>2</sub>. This measure confirms the recipe used to grow the passivation layer and shows the presence of dangling bonds, SiO<sub>x</sub>, that will be eliminated with the annealing under H<sub>2</sub>/N<sub>2</sub> atmosphere.



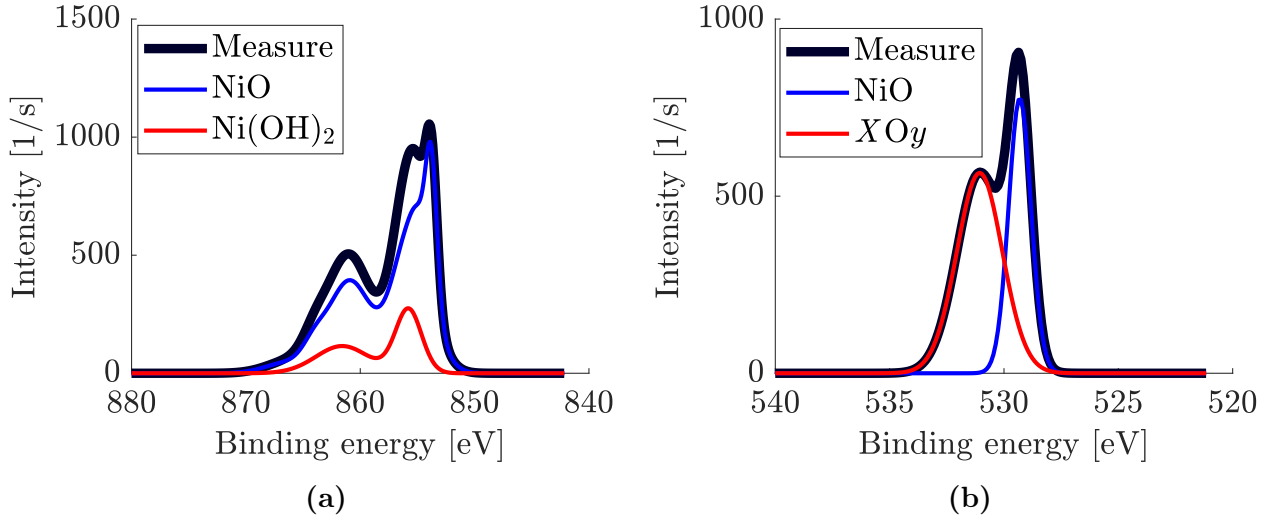
**Figure 4.2:** Measure and decomposition of the Si 2p for the native (a) and 3nm (b) SiO<sub>2</sub>.

For the first recipe of nickel oxide, only the composition is checked. The XPS survey is shown in Figure 4.3.



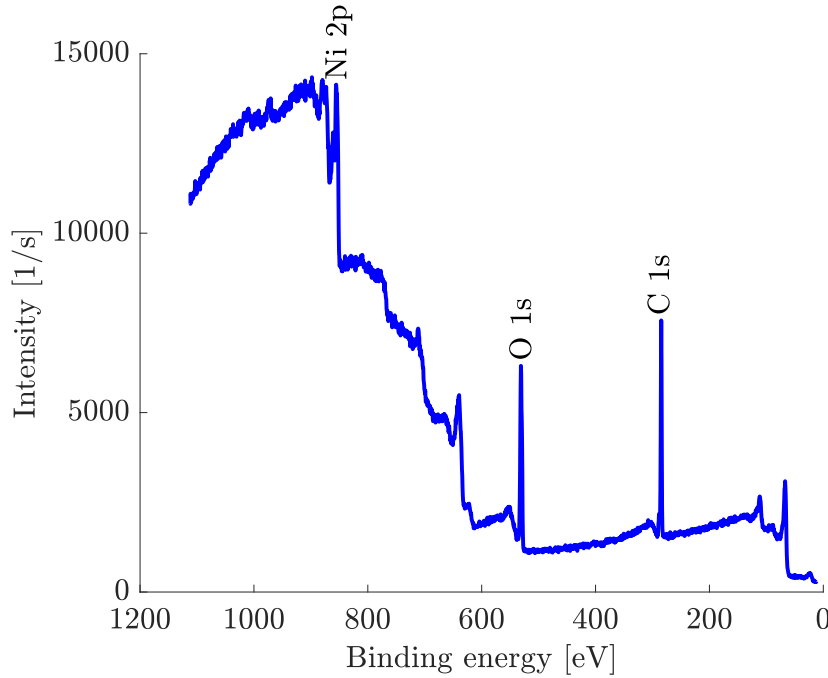
**Figure 4.3:** XPS analysis of NiO.

Figure 4.4 shows the decomposition done by software of the Ni 2p and the O 1s peak. There is a divergence between the two. For the first one, the software fitted the measurement with two different species: NiO and Ni(OH)<sub>2</sub>. However, for the oxygen balance, the oxygen measured is equal to the theoretical one only if the hydroxide is opted out. Thus, the recipe developed deposits a good nickel oxide with possibly a bit of hydroxide.



**Figure 4.4:** Measure and decomposition of the Ni 2p (a) and the O 1s (b) for the classic recipe of NiO. The blue line represents different oxide or hydroxide.

Finally, the NiO done by metal layer oxidation is also analysed (see Figure 4.5). Unfortunately, even though the deposited nickel is only 3nm, the silicon peak (around 67 eV) is not detected. It is thus impossible to measure the remaining metallic nickel. This will be discussed further.

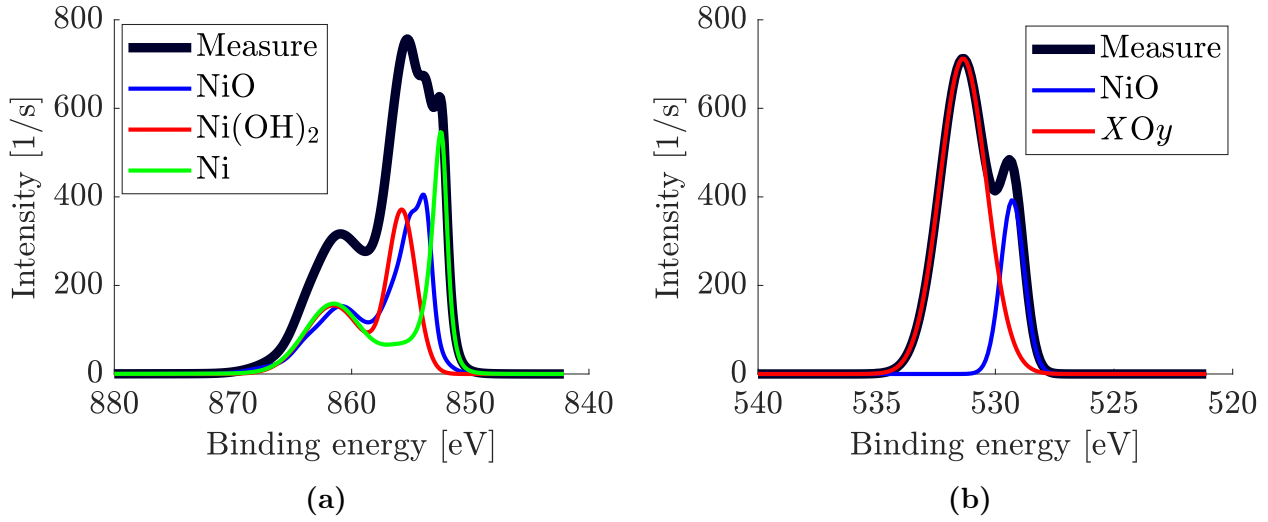


**Figure 4.5:** XPS analysis of NiO done by MLO.

Figure 4.6a indicates that not all the deposited nickel oxidised. Using the technique described earlier, the thickness of NiO can be approximated around  $1.5(\pm 0.3)$ . It is concordant with the literature (0.8-1.1nm) and to oxidise the whole 3nm, the temperature has to be risen (at least 340°C) [44].

Both graphs in Figure 4.6 also suggest a more significant proportion of Ni(OH)<sub>2</sub> (or NiOOH) in the sample. It can be lessened by reducing the pressure inside the chamber during the oxidation

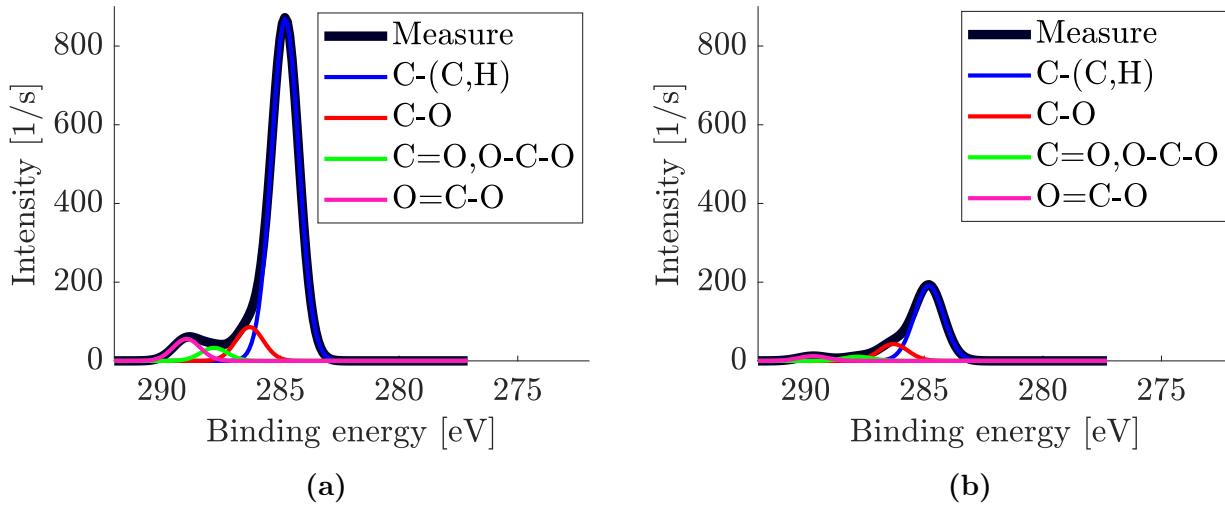
phase [45].



**Figure 4.6:** Measure and decomposition of the Ni 2p (a) and the O 1s (b) for the MLO recipe of NiO. The blue line represents different oxide or hydroxide.

Theoretically, the XPS analyse at a depth up to 10nm. With an oxide of 1.5nm and the rest of metallic nickel (less than 3nm), the technique should detect the silicon below.

However, a substantial carbon contamination measuring a few nanometers at the surface is disturbing the measurement. Around 50% of the detected atoms are carbon. Figure [4.7] presents a comparison with the SiO<sub>2</sub> 3nm where the contamination is lower.



**Figure 4.7:** Measure and decomposition of the C 1s peak for the MLO recipe of NiO (a) and the SiO<sub>2</sub> 3nm (b).



### 4.1.2 Crystallinity

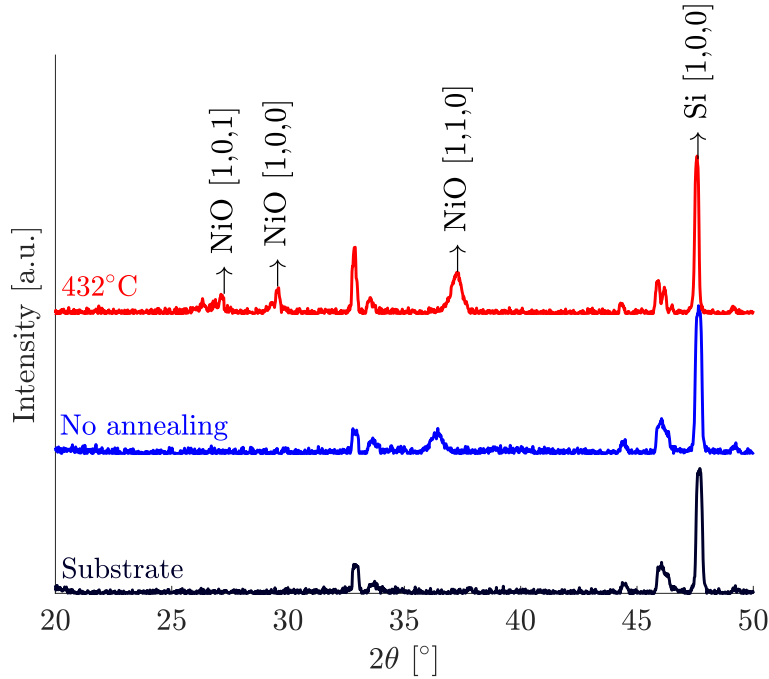
As explained in the method chapter, only the samples with 50nm of oxide are analyzed:

- NiO no annealing
- NiO annealing 432°C
- WO<sub>3</sub> no annealing
- WO<sub>3</sub> annealing 200°C
- WO<sub>3</sub> annealing 432°C
- WO<sub>3</sub> annealing 800°C

Unfortunately, the WO<sub>3</sub> no annealing and 200°C are not done due to a manipulation error.

For both samples, a clean wafer is first measured to have a basis for comparison.

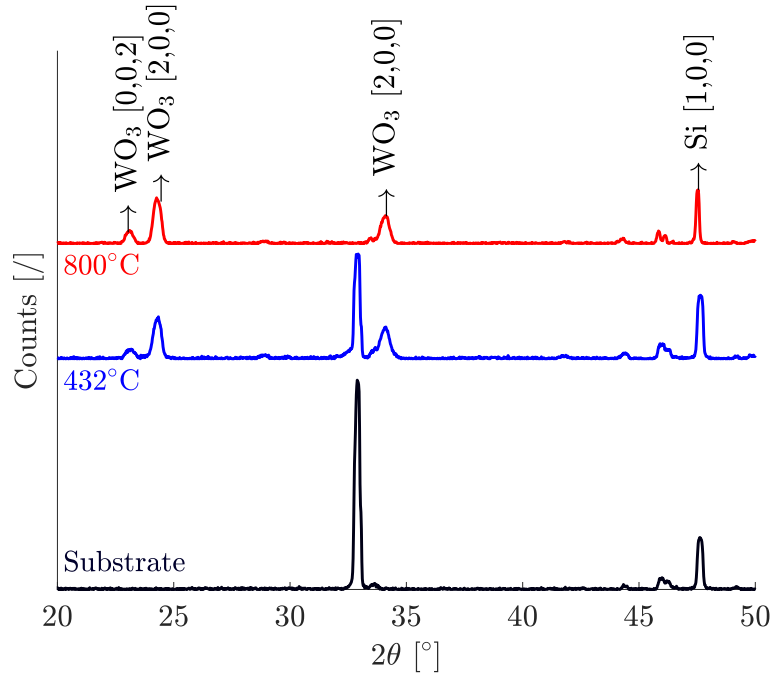
Figure 4.8 presents the result for the nickel oxide with some information about different peaks (not exhaustive). A small peak appears around 36° that reveal a small structure after the deposition. After the annealing at 432°C, this peak is intensified and others appear between 25 to 30°, confirming a crystallisation.



**Figure 4.8:** XRD analysis of NiO.

As for the tungsten oxide (see Figure 4.9), some data are missing, but the intensity of the different peaks coming from the oxide does not seem to change between the two annealings (432 and 800°C). However, the intensity of the silicon peak at 33° seems to diminish as the temperature rise.

This modification might come from different changes at the interface between the silicon and the oxide. For example, the oxygen can migrate and form a layer of SiO<sub>2</sub>, the other atoms can form tungsten silicide (W<sub>5</sub>Si<sub>3</sub>) and the WO<sub>3</sub> can also intermix with the silicon [46], [47]. All of this can change the structure and disturb the measure.

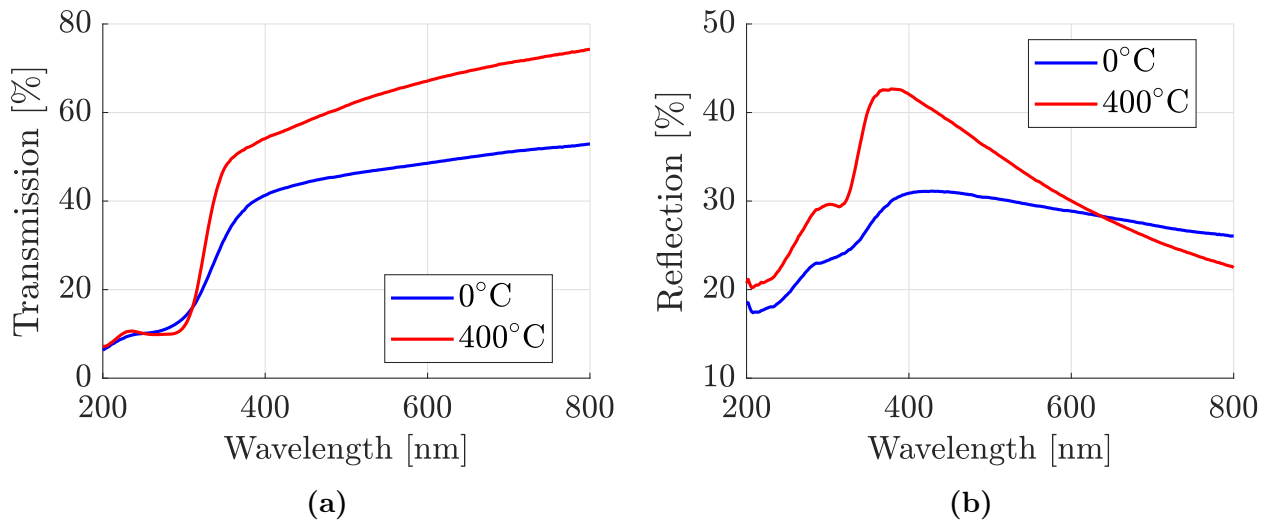


**Figure 4.9:** XRD analysis of  $\text{WO}_3$ .

#### 4.1.3 Bandgap

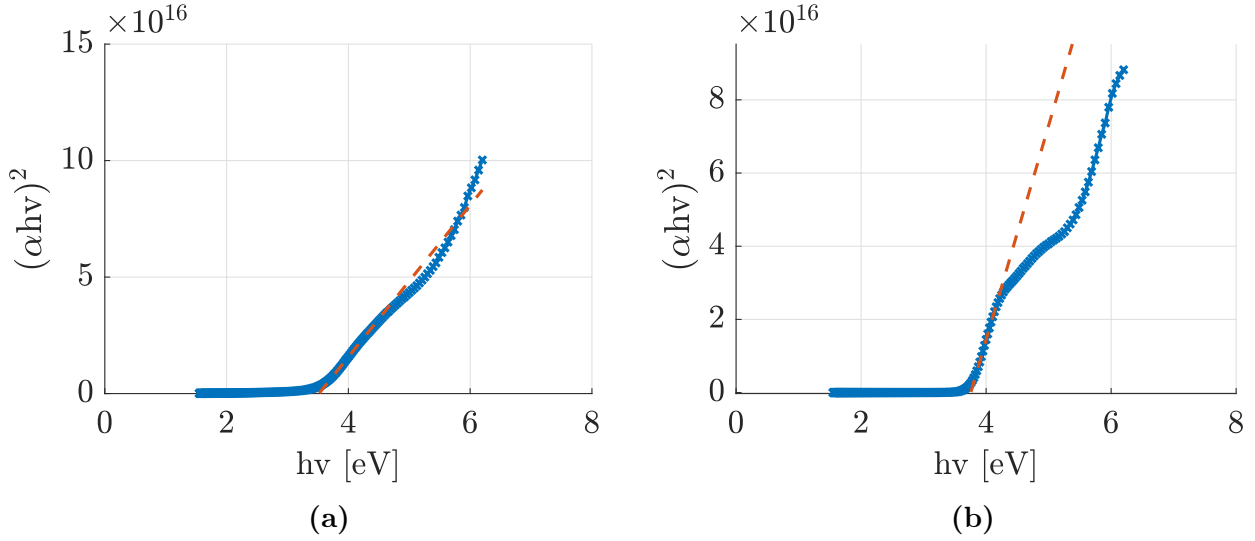
As explained earlier, the Tauc method is used to determine the bandgap and the influence of the annealing. Figure 4.10 presents the transmission and reflection for the nickel oxide. These characteristics were not measured for the substrate (fused quartz) alone due to a lack of materials, but it is transparent at the studied wavelengths.

The different curves have a transition around 300nm attesting the position of the bandgap. Since the transition after the annealing is sharper, it indicates the presence of less defects in the material. It can be the crystallisation rearranging the structure with also the diminution of dangling bonds tanks to the hydrogen during the annealing.



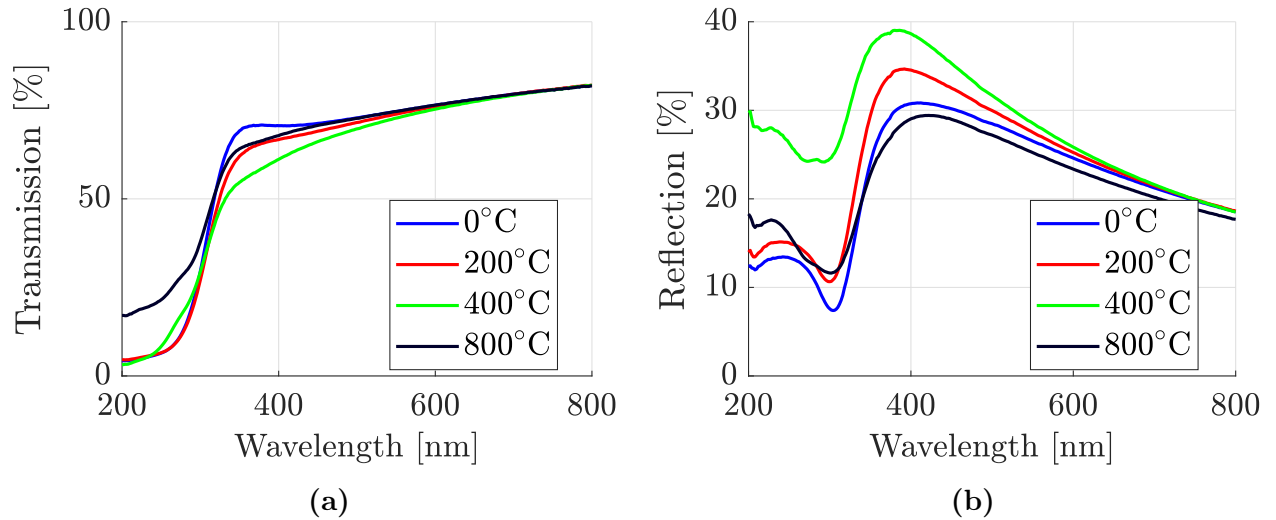
**Figure 4.10:** Transmission (a) and reflection (b) of 50nm nickel oxide on quartz.

The Tauc plot is shown in Figure 4.11 with the linear regression to calculate the bandgap. The two transitions are direct ( $n=1/2$ , see Equation (17)) with a bandgap of 3.52eV with no annealing and 3.75 with one at 432°C. The evolution concurs with different measurements from the literature [48]–[51].



**Figure 4.11:** Tauc plot of 50nm nickel oxide on quartz with no annealing (a) and one at 432°C (b). The dashed lines are a linear regression of the linear part to calculate the bandgap.

Figure 4.12 presents the different results for the tungsten samples. The sharp decline is still around 300nm, but the annealing does not seem to affect the slope of the transition, contrary to NiO.



**Figure 4.12:** Transmission (a) and reflection (b) of 50nm tungsten oxide on quartz.

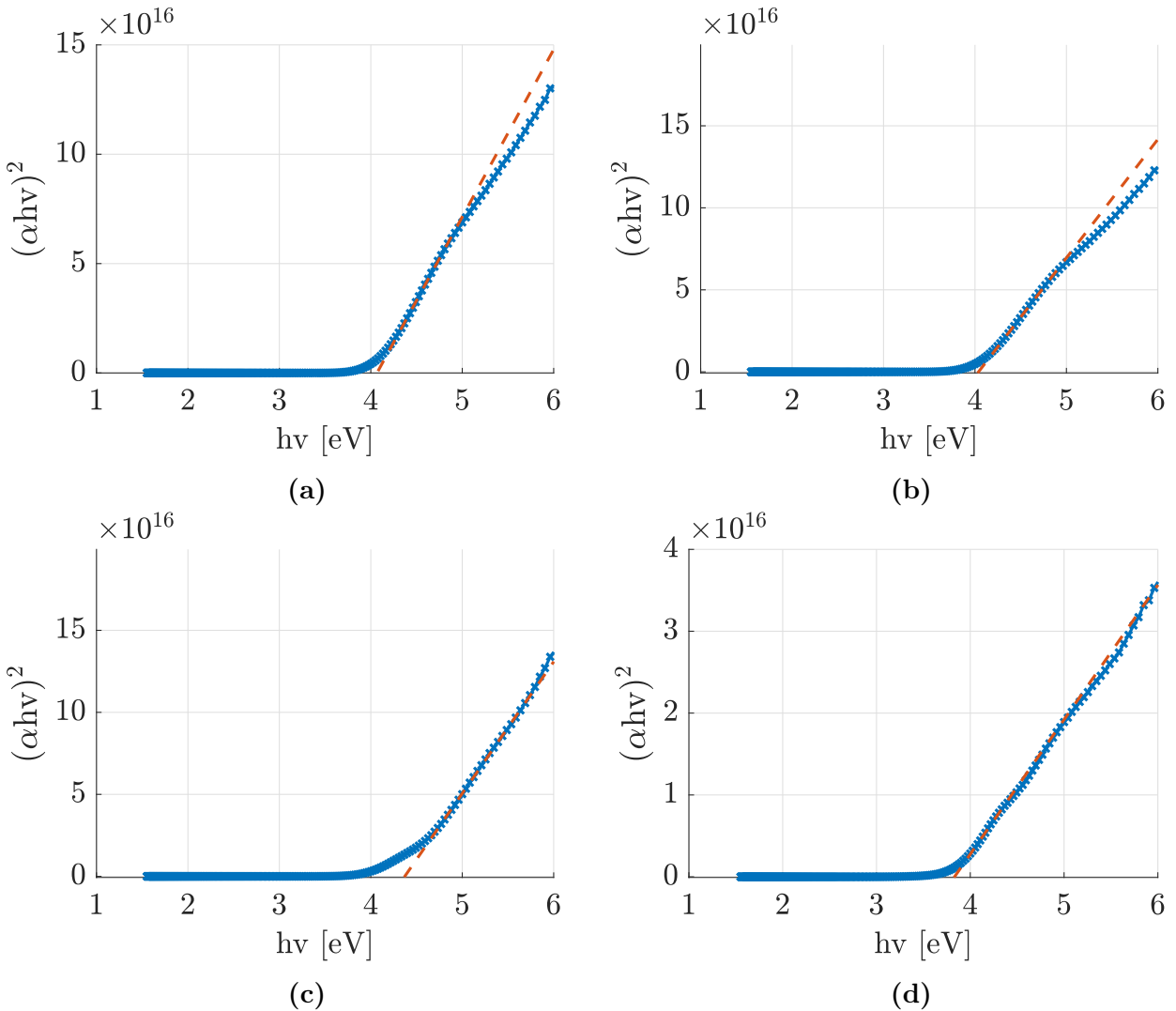
The transition is also direct with a bandgap changing with the annealing:

- No annealing: 4.1eV
- Annealing at 200°C: 4.0eV
- Annealing at 432°C: 4.4eV
- Annealing at 800°C: 3.8eV

The tendency of reduction of the bandgap is confirmed in the literature [52]–[54], but the values are lower ( $E_g = 2.6\text{--}3.2\text{ eV}$ ). It depends on the deposition method and the stress inside the thin film [55].

This may also explain the change in trend at 432°C. The annealing will first diminish the strain but rise around 400°C to go down after due to a change in the crystal size. The change in strain will affect the bandgap by increasing it [56].

To confirm this theory, the samples need more measurements (ex: Stoney) to measure the stress and the strain inside the thin oxide film.



**Figure 4.13:** Tauc plot of 50nm tungsten oxide on quartz with no annealing (a), one at 200°C (b), 432°C (c) and 800°C (d). The dashed lines are a linear regression of the linear part to calculate the bandgap.

## Mobility

To get the mobility of the different samples, two techniques are tested. The first one is the hall technique. There are 10 data points per sample and the mobilities obtained are all below  $0.3 \text{ cm}^2/\text{V.s}$  in absolute value (except for a few outliers), the detection limit (an example is presented in the Appendices). Thus, the mobility of NiO and  $\text{WO}_3$  is below it and it concords with the literature [57], [58].

A second technique with a lower detection limit is attempted: the Mott-Schottky in solution. The technique is used to measure the changes that occur in an electrochemical interface and is able to extract smaller mobility. Unfortunately, there was a problem with the substrate being too resistive who prevented the measurement. Even though the wafer was doped at  $1\text{-}10 \text{ }\Omega\text{.cm}$ , the resistance was above  $1 \text{ k}\Omega$ . Therefore, the investigation did not go further but a solution could be to deposit on a sheet of copper to have a lower resistivity.

### 4.1.4 Summary

To conclude, different techniques were used to characterise the different samples created or to confirm/measure what have been deposited in Winfab.

The first technique used was the XPS. It has allowed to determine the atoms species present at a depth of approximately  $10\text{nm}$ . To measure a thin layer within this  $10\text{nm}$ , the layer on which it rests has to be probed. It was used to measure the thickness of native  $\text{SiO}_2$  ( $1.2\text{nm}$ ) and confirm the thickness of the one that grew in Winfab ( $2.9\text{nm}$ ). It has also confirmed the deposition by reactive sputtering of suitable nickel oxide, with a small presence of hydroxide. In addition, the metal layer oxidation (MLO) recipe was checked. It was found that the recipe did not oxidise completely the nickel deposited (only  $1.5\text{nm}$  for  $3\text{nm}$  of Ni deposited), and there was the presence of more hydroxide. Some solutions were proposed to improve the process, like the deposition at a higher temperature and lower pressure.

The second technique used was the XRD to check the crystallinity of the metal oxide in function of the annealed temperature. For the NiO, it was found that some orders were present after the deposition and crystallinity rise with temperature. For the  $\text{WO}_3$ , crystallinity does not seem to change as the diffraction intensity of tungsten oxide is not changed between  $432$  and  $800^\circ\text{C}$ . However, a silicon peak present at  $37^\circ$  diminished with the temperature to disappear at  $800^\circ\text{C}$ . Thus, it could indicate some changes at the interface, like the formation of tungsten silicide or  $\text{SiO}_2$ . This change can be present only on this type of stack because the two others have an  $\text{SiO}_2$  layer between the silicon and the  $\text{WO}_3$ .

The third was to determine the bandgap using the tauc method. The NiO started at  $3.52$  and climbed at  $3.75\text{eV}$  with the annealing, and the transition was direct. As for the  $\text{WO}_3$ , the transition was also direct, but the bandgap trend decreases with the temperature. Except for the one annealed at  $432^\circ\text{C}$  but the stress inside the film can explain it [56]. The values found were between  $3.8$  and  $4.1\text{eV}$  and they are higher than the ones found in the literature. Again, the stress due to the deposition may explain it but more measurements are needed.

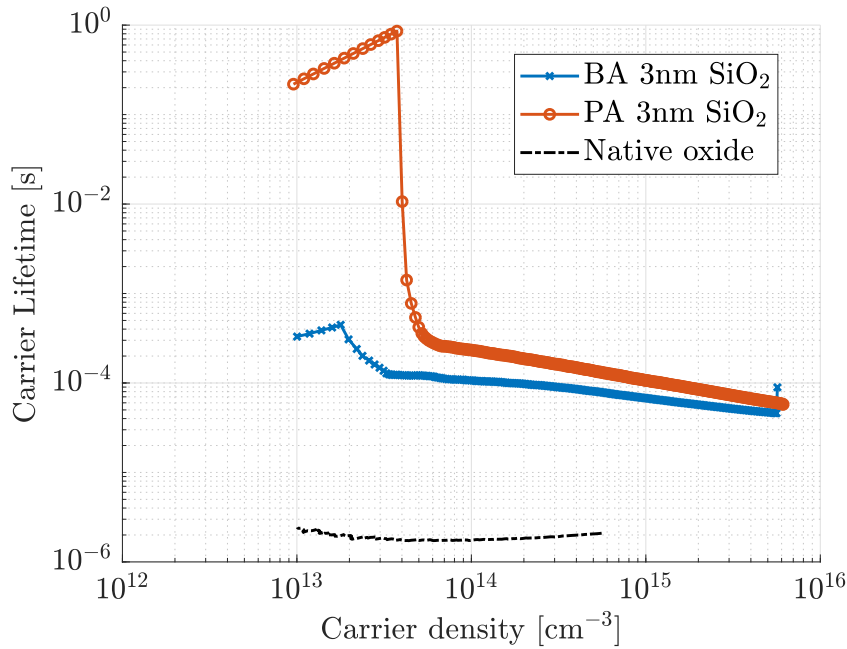
About the two last different techniques, it was to measure the mobility. The first one, based on the Hall-effect, gave different values below its detection limit: between  $-0.3$  and  $0.3 \text{ cm}^2/\text{V.s}$ . Thus, the mobility was under those values. A second technique was the triad, the Mott-Schottky in solution. Its detection limit was well below what was expected, but a problem with the silicon wafer resistivity prevented the measure.

## 4.2 Performance - Passivation and selective layer

### 4.2.1 Lifetime

Different measures were performed during the process to investigate the impact of the process on the lifetime.

First, a simple wafer was measured to track the impact of the different processes. Then, a silicon wafer after the growth of  $\text{SiO}_2$  was measured before and post-annealing (BA and PA) under  $\text{H}_2/\text{N}_2$  atmosphere. The results are presented in Figure 4.14 and Table 10 for the result at an injection level of  $5 \cdot 10^{15}$  (when possible).

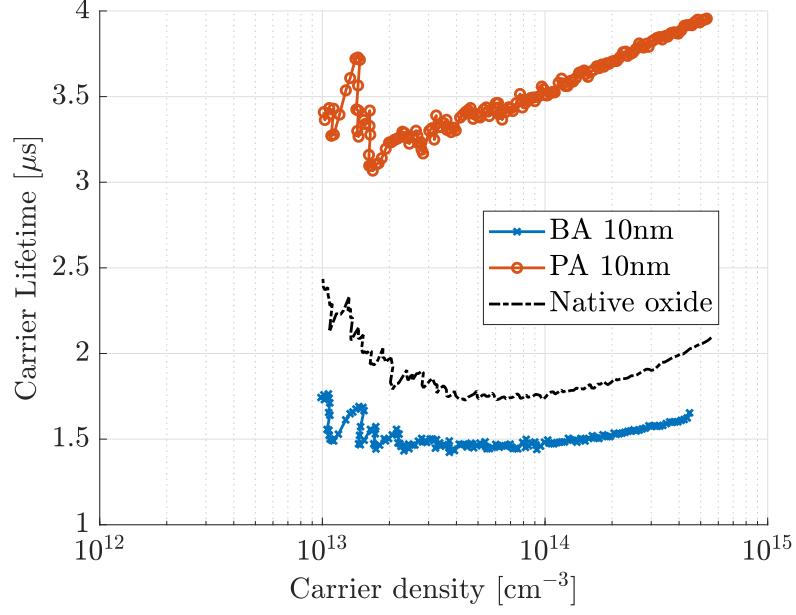


**Figure 4.14:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the  $\text{SiO}_2$  3nm before/post annealing (BA and PA).

|                       | $\tau_{eff}$ ( $\mu\text{s}$ ) | $S_{eff}$ (cm/s) | Reported values (cm/s) [59] |
|-----------------------|--------------------------------|------------------|-----------------------------|
| Native oxide          | 2                              | 8600             | /                           |
| $\text{SiO}_2$ 3nm BA | 46                             | 383              | /                           |
| $\text{SiO}_2$ 3nm PA | 62                             | 290              | 10-400                      |

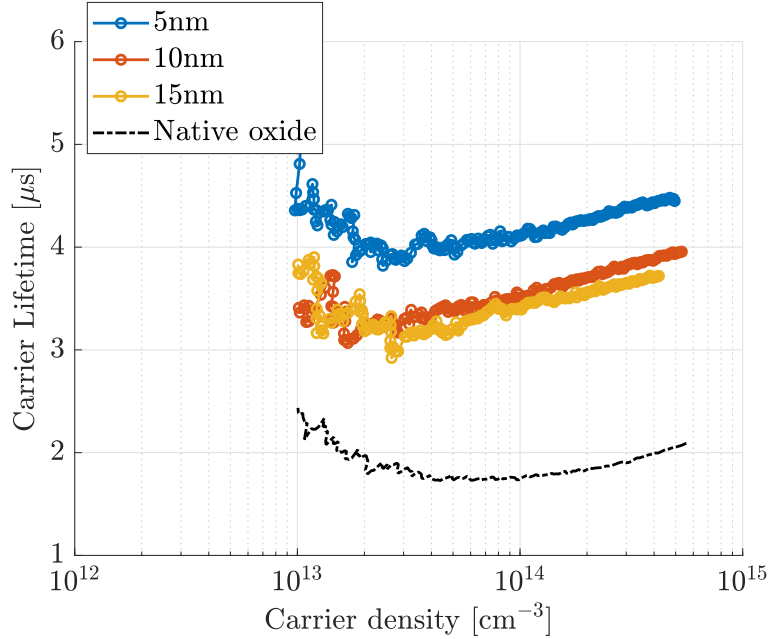
**Table 10:** Summary of the results the native oxide and the  $\text{SiO}_2$  3nm before/post annealing (BA and PA) at an injection level of  $5 \cdot 10^{15}$  (when possible).

Then for the NiO, the different depositions were done on both sides of the wafer and also measured before and post-annealing at  $432^\circ\text{C}$  (see Figure 4.15, the others are in the Appendices). It confirms the necessity of the annealing by doubling the lifetime of the minority carrier by neutralizing the defect caused by the dangling bond: at an injection level of  $1 \cdot 10^{14}$ , it starts at 1.5 to go at  $3.5 \mu\text{s}$ .



**Figure 4.15:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the NiO 10nm before/post annealing (BA and PA).

Even though the annealing improved the lifetime, the deposition still greatly decreases compared to the wafer with just a layer of  $\text{SiO}_2$ . With almost no influence of the layer thickness, see Figure 4.16 and Table 11 (the injection level is different from the result above). The surface recombination velocity result are quite high compare to commercial solar cell ( $\approx 70$  cm/s) [60]. However, comparing with only metal on silicon ( $>1\text{E}5$  cm/s) is an improvement [61]. Lastly, it has to be noted that the result for commercial solar cell used a higher quality wafer with less defects and an higher lifetime.

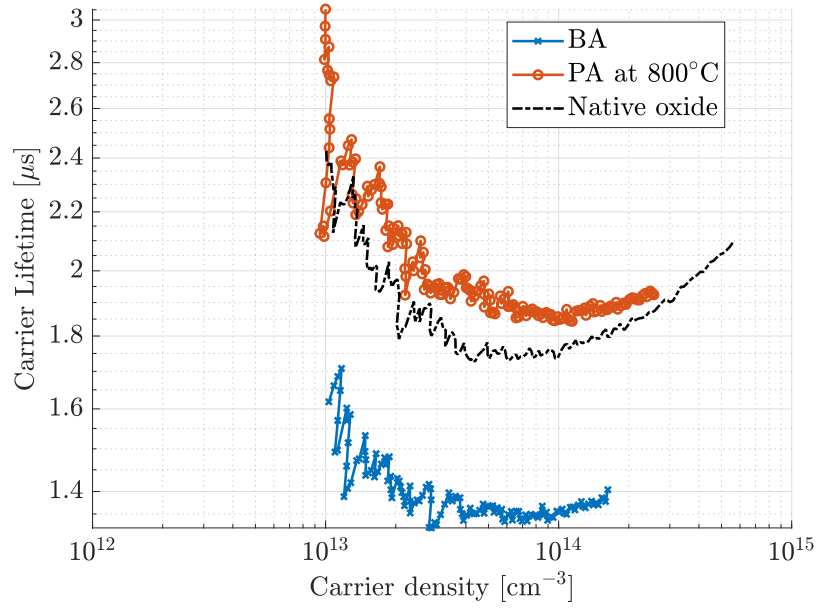


**Figure 4.16:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the NiO (5,10 and 15nm)post annealing. The  $\text{SiO}_2$  is not shown for clarity.

|                      | $\tau_{eff}$ ( $\mu s$ ) | $S_{eff}$ (cm/s) | Reported values<br>(cm/s) [21], [59] |
|----------------------|--------------------------|------------------|--------------------------------------|
| Native oxide         | 2.1                      | 8600.1           | /                                    |
| SiO <sub>2</sub> 3nm | 234.0                    | 77.0             | 10-400                               |
| NiO 5nm              | 4.1                      | 4380.5           | /                                    |
| NiO 10nm             | 3.5                      | 5130.3           | 225 ( $\approx 80 \mu s$ )           |
| NiO 15nm             | 3.4                      | 5284.7           | /                                    |

**Table 11:** Summary of the results the native oxide, the SiO<sub>2</sub> 3nm and the NiO post-annealing at an injection level of  $1 \cdot 10^{14}$ . Careful, the injection level is different from the previous table and the reported values.

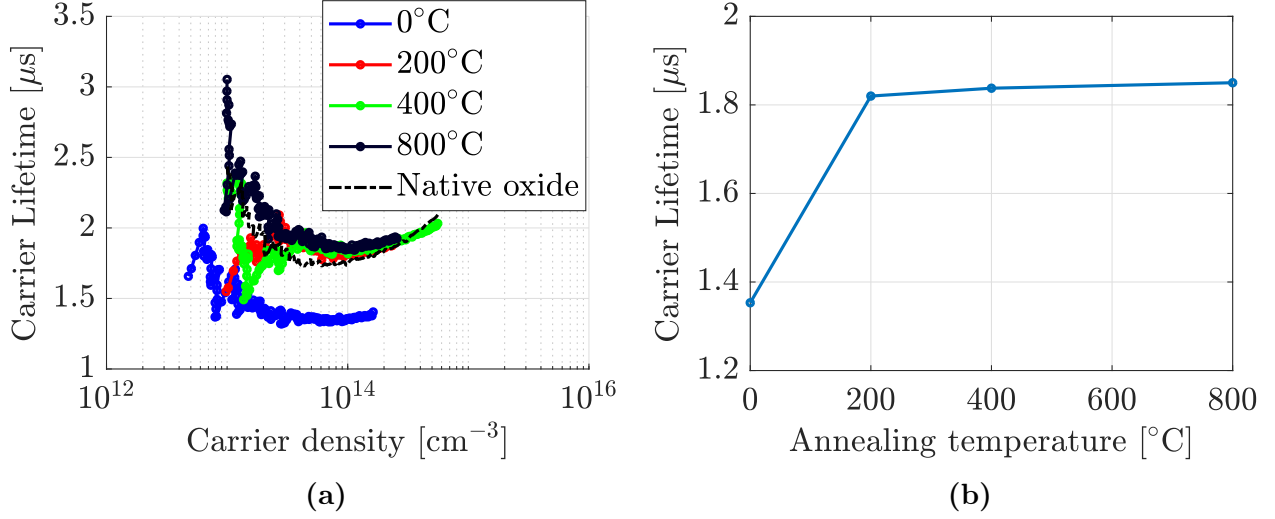
The tendencies are the same but lowered for the WO<sub>3</sub>. The annealing still nearly doubles the lifetime but with a final result below the NiO:



**Figure 4.17:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the WO<sub>3</sub> before/post-annealing (BA and PA) at 800°C.



Moreover, the different annealing (200, 432 and 800°C) has a limited influence after 200°C on the lifetime:



**Figure 4.18:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the WO<sub>3</sub> post annealing (0, 200, 432 and 800°C) (a). And the carrier lifetime versus the annealing temperature at an injection level of 1\*10<sup>14</sup> (b). The SiO<sub>2</sub> is not shown for clarity.

There is a huge difference between the lifetime measured and the ones found in diverse literature. Since the value also drops after the deposition, 234 to 3-4 μs for the NiO and below 2 for the WO<sub>3</sub> (SRV: ≈9700 cm/s), many defects are created during it. When the oxygen enters the deposition chamber, it is ionized negatively in the plasma. Then, the negative charge is attracted to the anode, where the wafer is, at considerable speed, creating a considerable amount of defects.

To test this theory, the SiO<sub>2</sub> 3nm wafer was introduced into an O<sub>2</sub> plasma descum resist stripper for one minute to simulate the ion bombardment. The lifetime has indeed been reduced around 2 μs, the result before the annealing for the different NiO wafers.

Thus, the lifetime's difference between the 3 NiO samples can be explained by the fact that the wafer with the higher thickness spent more time in the deposition chamber under the ion bombardments. The results of the WO<sub>3</sub> concur with this theory because, even though they are annealed at different temperatures, the lifetime stays the same: the samples spent the same time inside the deposition chamber.

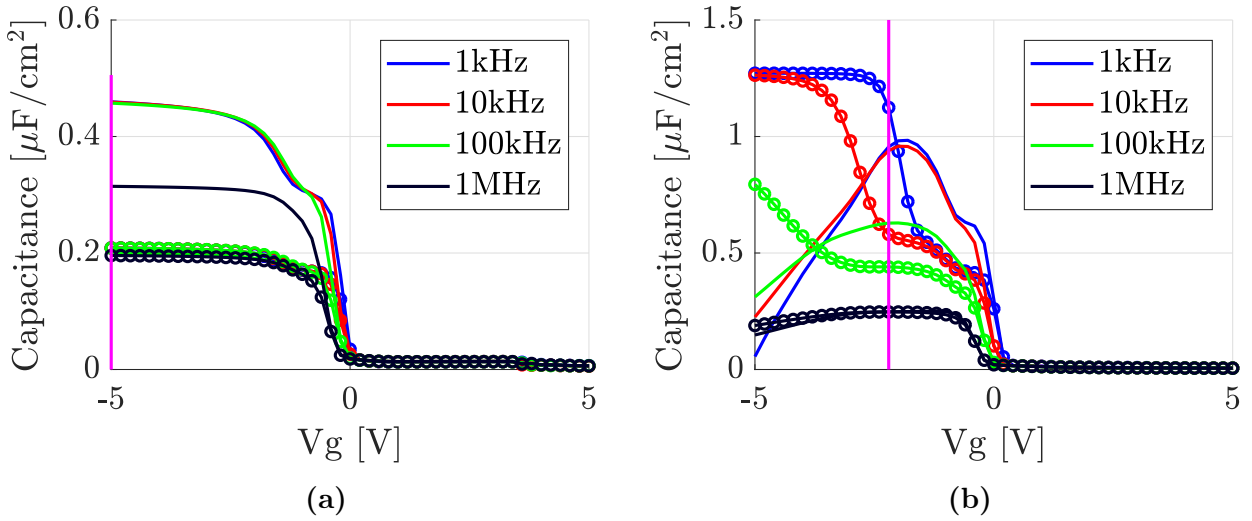
Finally, the NiO seems better than WO<sub>3</sub> but one needs to be careful with this. It could come from their different parameters during deposition. For example, the plasma for the tungsten deposition has a higher energy (100W) than the NiO (50W). Thus, the defect due to oxygen ion can be greater for the WO<sub>3</sub>, even though it spent less time in the deposition chamber.

Onishi et al. [62] confirm the negative impact of negatively charged ions during the deposition. Since tungsten and nickel oxide depositions are only possible in sputtering in Winfab, a new recipe was tried with the oxidation decoupled from the deposition called the metallic layer oxidation [25]. Unfortunately, as explained in Section 4.1.1, the oxidation was not complete. Thus no electrical measurements were made with this deposition technique.

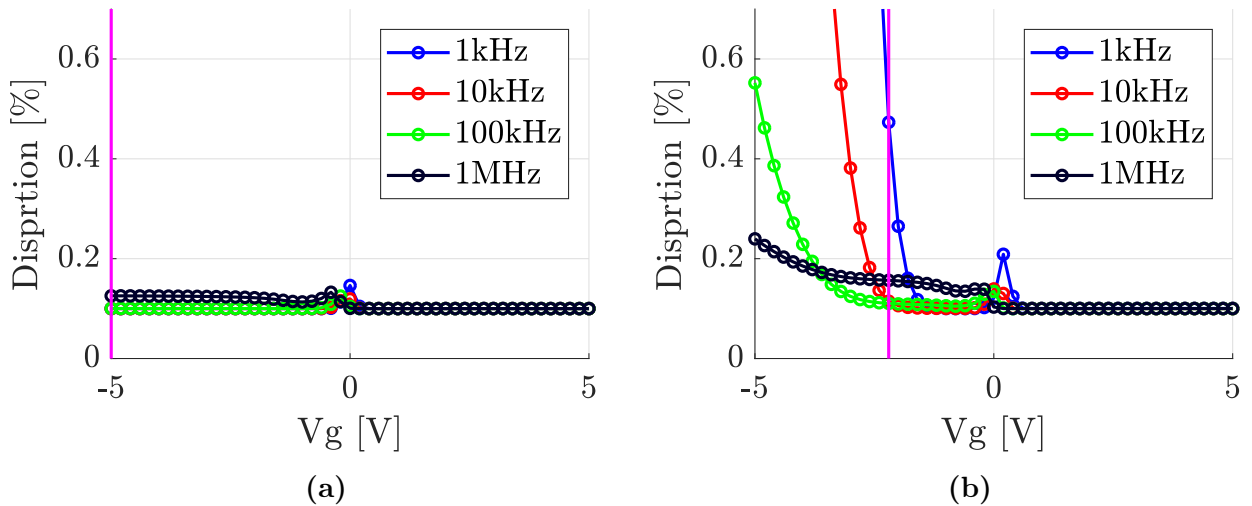
### 4.2.2 CV measurement

#### The different trends

As explained in the method chapter, the CV measurements first need to be corrected using the 6 elements model (see Figure 4.19) and the dispersion has to be checked (see Figure 4.20). The correction is not perfect, especially for the NiO, but the series resistance effect is diminished by regrouping the different curves. Therefore, for the rest of the section, only the corrected curves will be used. The purple vertical line indicates when the dispersion is greater than 0.5% (on the left), where the accuracy of the measure is not assured. The fluctuation on Figure 4.19a can be explained by the important dispersion that will alter the capacitance measurement. The different curves not presented in this chapter can be found in the appendix.

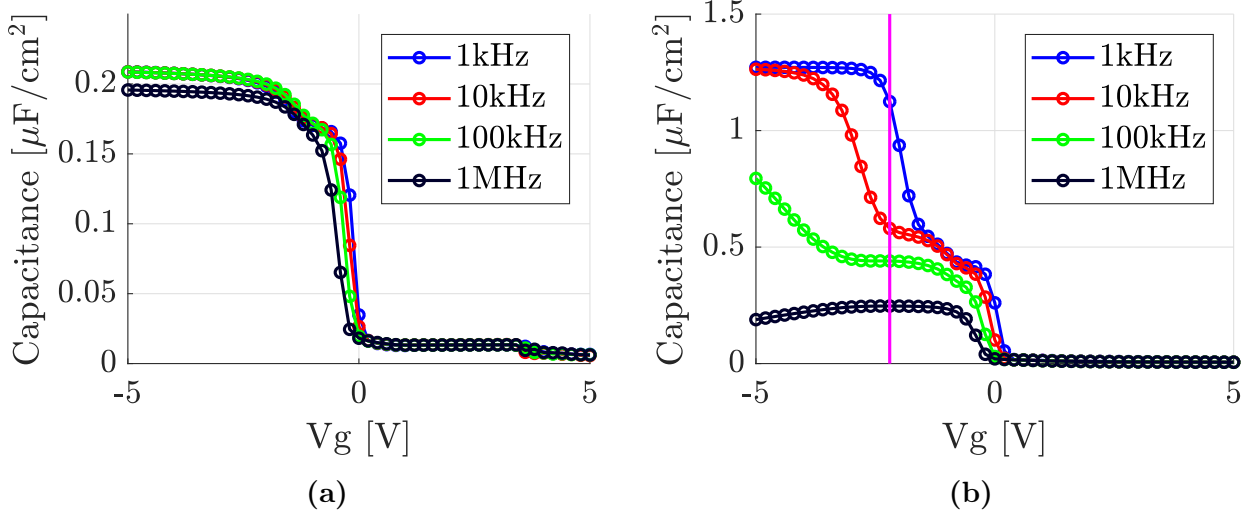


**Figure 4.19:** Capacitance-voltage measurements with their respective correction for  $\text{WO}_3$  annealed at  $800^\circ\text{C}$  (a) and NiO 5nm (b). The marked lines are the corrections, while the others are the actual measurements. The right of the purple line indicates a dispersion below 0.5%.



**Figure 4.20:** Dispersion for  $\text{WO}_3$  annealed at  $800^\circ\text{C}$  (a) and NiO 5nm (b). The right of purple line indicates a dispersion below 0.5%.

Figure 4.21 presents one result of each NiO and WO<sub>3</sub> sample. The first noticeable characteristic is the shift of the flat band voltage ( $V_{fb}$ ) for both. A. Mazurak et al. [63] present different possibilities to explain the move.

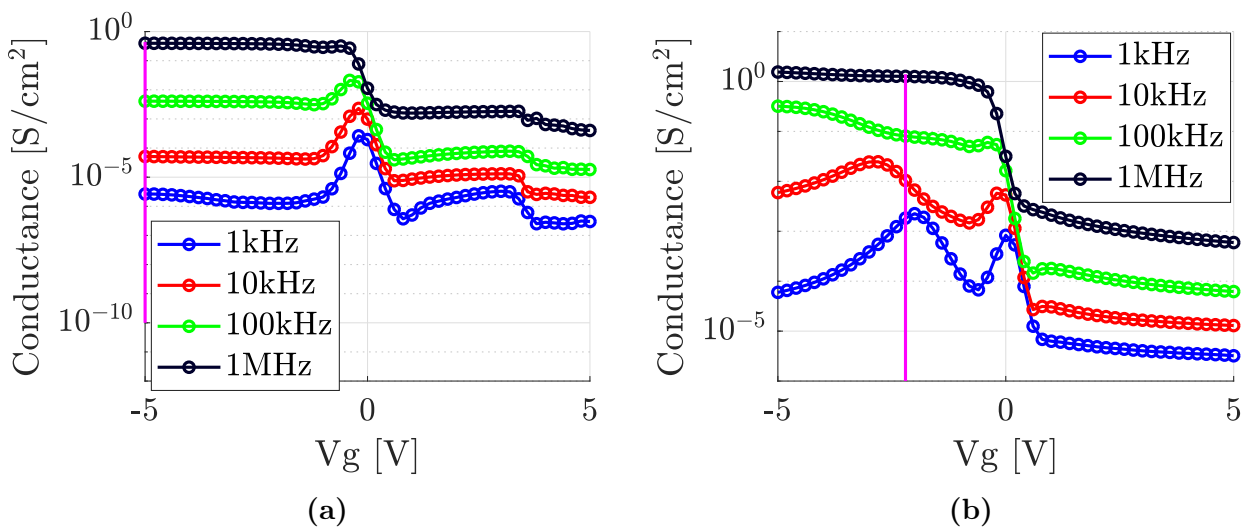


**Figure 4.21:** Capacitance-voltage corrected measurements for WO<sub>3</sub> annealed at 800°C (a) and NiO 5nm (b). The right of purple line indicates a dispersion below 0.5%.

The first dismissed explication is the traps frequency response. Since the curves are rather smooth, a high concentration of traps responding to the ac signal is unlikely.

An other possibility is a change of the electrical permittivity. However, the phenomenon is too marked to be the sole explication.

By looking at the leakage conductance of the structure, it is possible to found another explication (see Figure 4.22).



**Figure 4.22:** Capacitance-voltage corrected measurements for WO<sub>3</sub> annealed at 800°C (a) and NiO 5nm (b). The right of purple line indicates a dispersion below 0.5%.

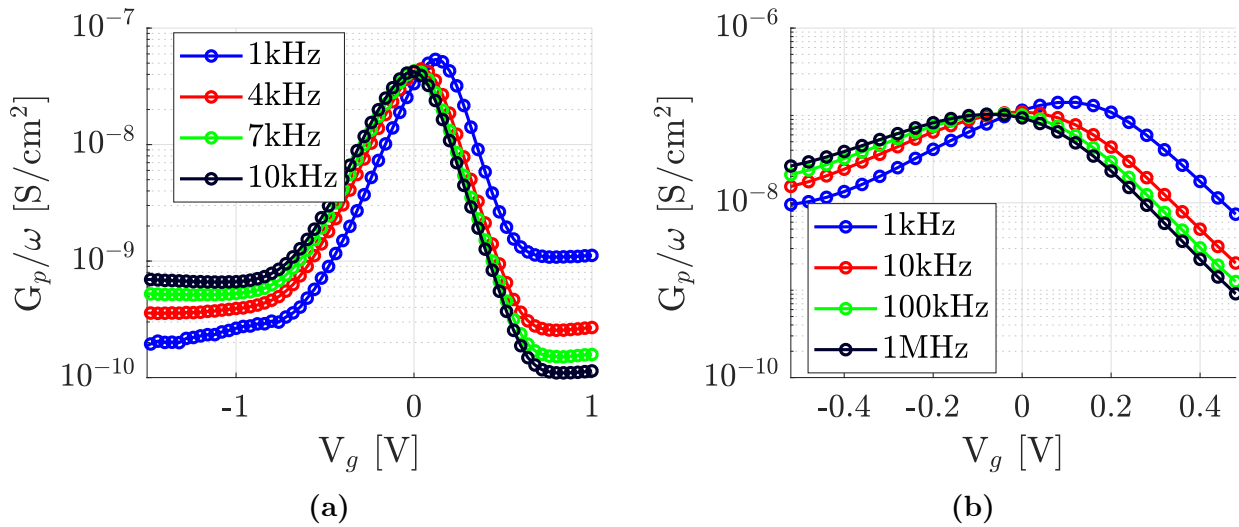
The same trends are found in the paper (the conductance near the flat-band voltage increase linearly with the frequency). A. Mazurak et al. suppose, thanks to this measure and others that are not done in this work, that more and more majority carriers are trapped in the oxide stack due to a leakage mechanism while the frequency increase. If there are more charges in the oxide, the positive contributions of  $Q_{ox}$  rise and change the flat-band voltage, with all the other parameters kept constant.  $\Phi_{MS}$  is the work-function between the mercury probe and the silicon):

$$V_{FB} = \Phi_{MS} - \frac{Q_{ox}}{C_{ox}}$$

However, more measures are needed to fully explain the different mechanisms in play that change the flat-band voltage.

### Density of interface traps ( $D_{it}$ )

Now that the general trends of the CV measurements have been explained, different parameters can be extracted, like the density of interface traps ( $D_{it}$ ). Table 12 presents the result for the different samples with Figure 4.23 two graphs of  $G_p/\omega$ . The method used is explained in Section 3.3.1.



**Figure 4.23:** The corrected conductance divided by the frequency versus the voltage for  $\text{WO}_3$  annealed at  $800^\circ\text{C}$  (a) and  $\text{NiO}$  5nm (b).

| Samples               | $D_{it}$<br>( $\text{cm}^{-2} \text{ eV}^{-1}$ ) |
|-----------------------|--------------------------------------------------|
| SiO <sub>2</sub> 3nm  | $1.20 \cdot 10^{12}$                             |
|                       |                                                  |
| NiO 5nm               | $2.20 \cdot 10^{12}$                             |
| NiO 10nm              | $1.59 \cdot 10^{12}$                             |
| NiO 15nm              | $1.56 \cdot 10^{12}$                             |
|                       |                                                  |
| WO <sub>3</sub> 0°C   | $1.88 \cdot 10^{12}$                             |
| WO <sub>3</sub> 200°C | $1.78 \cdot 10^{12}$                             |
| WO <sub>3</sub> 432°C | $1.95 \cdot 10^{12}$                             |
| WO <sub>3</sub> 800°C | $8.40 \cdot 10^{11}$                             |

**Table 12:** The density of interface traps is calculated from the conductance method for the different samples, at the end of their own process.

For the silicon, the value is higher than the one reported in the literature for larger thickness ( $1 \cdot 10^{11}$ ) [59] and will impact the rest of the measure.

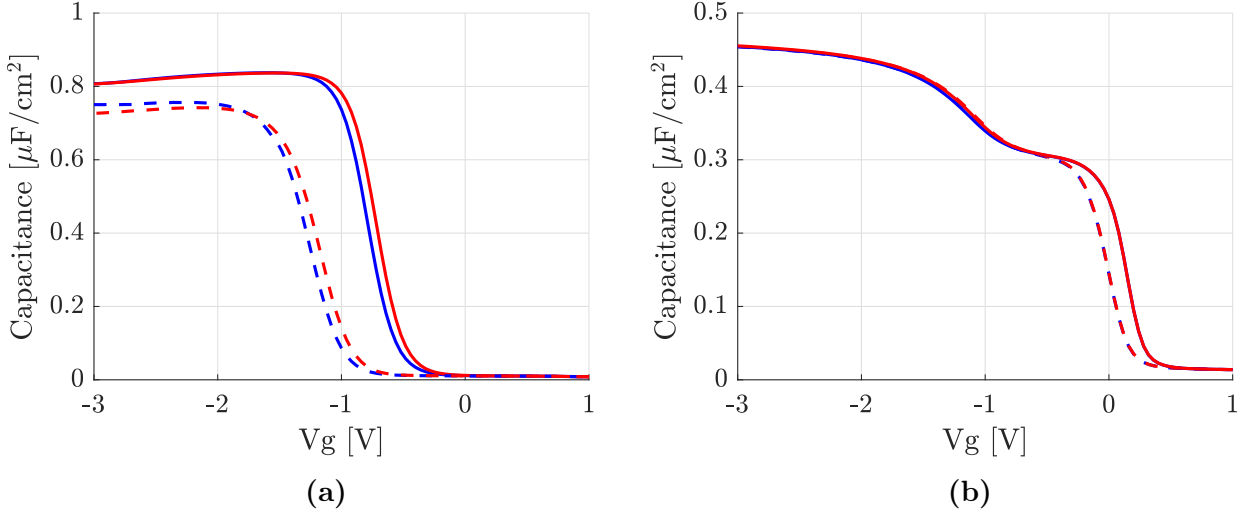
As expected, all the processes deteriorate the interface. For the NiO, the 5nm has a higher  $D_{it}$  for an unknown reason. Above 10nm, the thickness does not seem to influence it, and the interface's deterioration is minimal.

For the WO<sub>3</sub>, the density is globally higher than the NiO, but the annealing seems to decrease it. The difference between the two materials can be due to power differences during the deposition, as explained in the previous section.

For the WO<sub>3</sub> annealed at 800°C, it even goes lower than the SiO<sub>2</sub> with no deposited oxide. An explication can come from the annealed time because, due to logistical constraints, it has spent twice the time in the furnace (see the process sheet at Table 8). Thus, more measurements are required to extract the different parameters that impact the interface trap density and verify if this is not an outlier.

## Hysteresis

One last piece of information can be extracted from CV measurement: the mobile charge. Unfortunately, only the silicon and tungsten oxide samples were analysed. Figure 4.24 presents the WO<sub>3</sub> sample with no annealing, where the hysteresis curve is the most significant, and with the annealing at 800°C.



**Figure 4.24:** CV hysteresis measurements of  $\text{WO}_3$  with no annealing (a) and  $800^\circ\text{C}$  (b). The solid lines represent the measure at 1kHz and the dashed at 10kHz. The red indicates a measure negative to positive and the blue the opposite, positive to negative.

From Equation (8) in the method section, the mobile charge density is extracted from the different samples and summarize in Table 13.

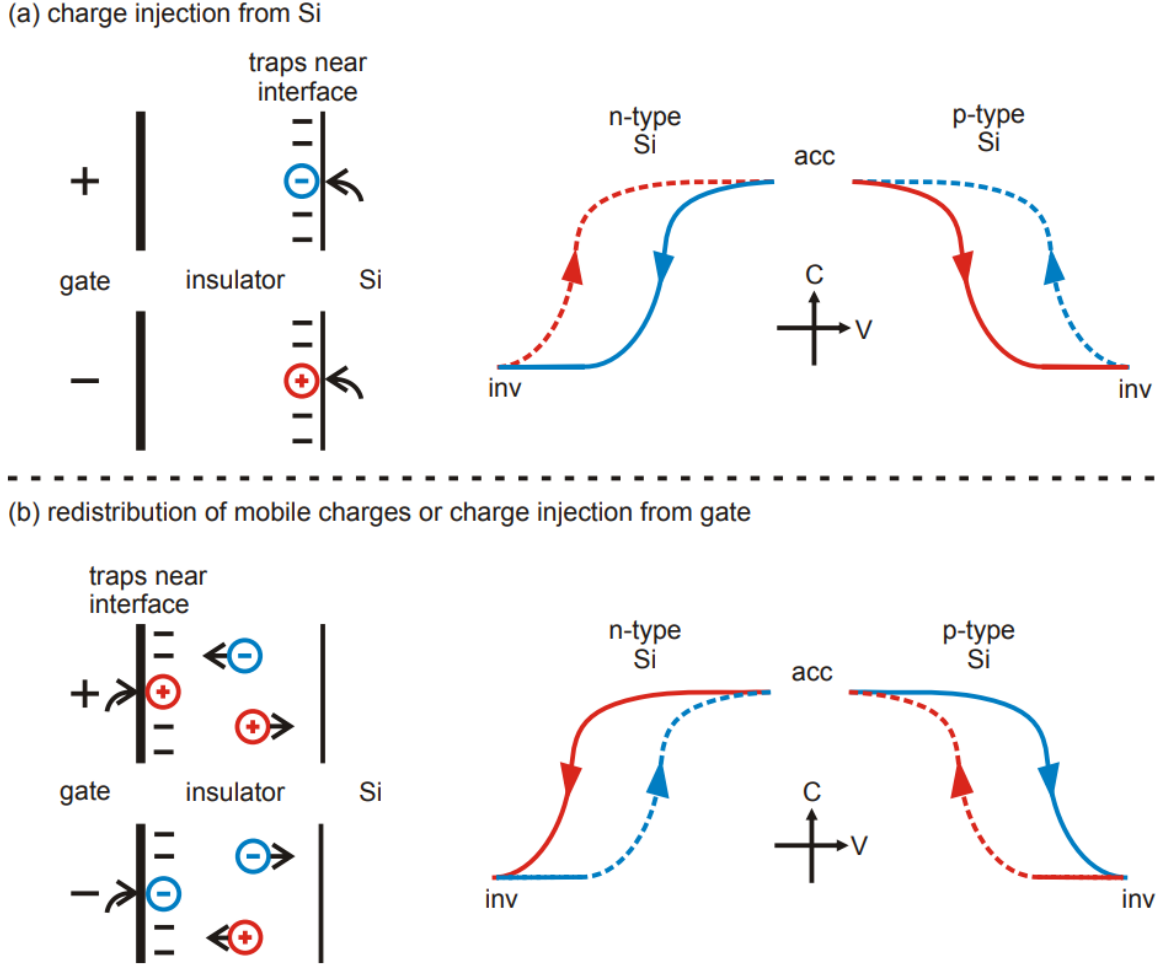
| Sample                            | $\Delta V_{fb}$ (V)   |                       | $N_t$ ( $\text{cm}^{-3}$ ) |                       |
|-----------------------------------|-----------------------|-----------------------|----------------------------|-----------------------|
|                                   | 1kHz                  | 10 Khz                | 1kHz                       | 10 Khz                |
| $\text{SiO}_2$ 3nm                | $-7.61 \cdot 10^{-2}$ | $-5.44 \cdot 10^{-2}$ | $-1.42 \cdot 10^{11}$      | $-9.92 \cdot 10^{10}$ |
| $\text{WO}_3$ $0^\circ\text{C}$   | $-6.87 \cdot 10^{-2}$ | $-7.36 \cdot 10^{-2}$ | $-1.13 \cdot 10^{11}$      | $-1.18 \cdot 10^{11}$ |
| $\text{WO}_3$ $200^\circ\text{C}$ | $7.08 \cdot 10^{-3}$  | $-5.42 \cdot 10^{-3}$ | $1.54 \cdot 10^{10}$       | $-8.70 \cdot 10^9$    |
| $\text{WO}_3$ $432^\circ\text{C}$ | $5.92 \cdot 10^{-3}$  | $6.70 \cdot 10^{-3}$  | $1.41 \cdot 10^{10}$       | $1.54 \cdot 10^{10}$  |
| $\text{WO}_3$ $800^\circ\text{C}$ | $3.35 \cdot 10^{-5}$  | $-1.38 \cdot 10^{-5}$ | $4.35 \cdot 10^7$          | $-1.79 \cdot 10^9$    |

**Table 13:** Summary of the results of the mobile charge concentration ( $N_t$ ) for the  $\text{SiO}_2$  3nm and the  $\text{WO}_3$  post annealing.

The first result is that mobiles charges come from the growth of  $\text{SiO}_2$  by dry oxidation and not the deposition. But, on the contrary, it does not seem to have a great impact on it.

What has an impact is the annealing at different temperatures. Since the hysteresis is caused by defects, the annealing under  $\text{H}_2/\text{N}_2$  atmosphere will passivate them, decreasing the mobile charge.

What is interesting in Table 13, is the change of sign between 1kHz and 10kHz. It indicates that two different mechanisms, showed in Figure 4.25, are at work.



**Figure 4.25:** Charge mechanisms responsible for C-V hysteresis formation of a MIS capacitor due to (a) charge injection from the Si and (b) redistribution of charges or charge injection from the gate. In this work, the gate is the drop of mercury and the insulator is  $\text{WO}_3$  then  $\text{SiO}_2$ .

From [64].

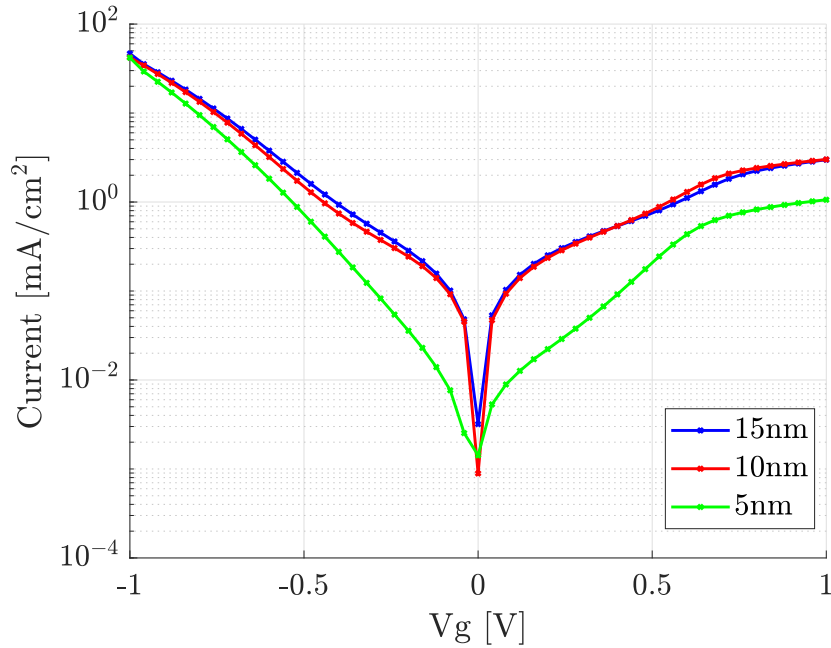
The first one (Figure 4.25.a) is the charge injection from the silicon into the traps near the interface  $\text{SiO}_2/\text{Si}$ . When the applied voltage is negative to the positive (for p-type wafer), majority charge carriers (holes) are attracted from the silicon into the traps near the interface. It increases the total positive charge,  $Q_{ox}$ , inside the oxide. Thus  $V_{fb}$  is shifted to the right. When it is positive to negative, the opposite happened. Electrons from the Si wafer are injected and trapped, leading to an increase of the total negative charge of  $Q_{ox}$ , shifting  $V_{fb}$  to the positive side. All of this is giving a counter-clockwise hysteresis.

For Figure 4.25.b, the concerned interface change (from insulator/Si to gate/insulator) and another phenomenon occurs. From negative to positive, the charge injection may still be present, but this time, it is the gate that injects electrons to traps at the interface. Furthermore, charge redistribution occurs when the negative mobile charges drift (or tunnel) towards the c-Si/insulator interface. All of this leads to an increase of the negative component of  $Q_{ox}$ , shifting the curve to the right. On the opposite, when the measure is done from the positive to the negative, holes are injected at the gate interface and/or the electrons are redistributed near the silicon interface, leading to an increase of the total positive charge of  $Q_{ox}$ , shifting  $V_{fb}$  to the negative side. All of this is, giving a clockwise hysteresis.

Of course, the two phenomena are not exclusive, and when a hysteresis appears, both can be present and one dominates. This is certainly what happens in the different samples where the sign change with the frequency: both mechanisms are detected. Both interfaces are probed at the lower frequency (1kHz), and the first mechanism (a) dominates. At the higher frequency (10kHz), fewer defects near the insulator/Si interface are probed, changing the dominant mechanism. It is different for the sample with no annealing ( $\text{WO}_3$  0°C in Table 13) since there are more defects in the oxide that have not yet been passivated. Thus, mechanism b dominates at both frequencies.

#### 4.2.3 IV measurement

Current-voltage measurements were done on the different stacks to assess the hole selectivity and understand the different conduction mechanisms. Unfortunately, the measure on the  $\text{WO}_3$  stack and just  $\text{SiO}_2$  did not work for unknown reasons. Even with a high range of voltage, -10 to 10V, the measured current was below 1pA. A problem with the prober was suspected but time was missing to investigate the issue. Thus, only the result for the different thicknesses of NiO is showed (see Figure 4.26) and discussed.



**Figure 4.26:** Current-voltage measurement for NiO and its different thicknesses.

The first noticeable trend is the asymmetry between the positive and negative tension. This proves a selective effect towards holes versus electrons due to the band diagram. The level of current at  $\pm 0.6\text{V}$ , typical tension for a solar cell, and their ratio are showed in Table 14. No precise trends for the selectivity versus the thickness is found. Nevertheless, the current seems to rise with the thickness while the opposite is expected. It may indicate an oxide deterioration during the deposition process and thus, be related to what was explained in the Section 4.2.1: ion of oxygen are accelerated towards the wafer, creating defects. Since the deposition time rises to deposit a thicker oxide, more defects are created, leading to increased conductivity.



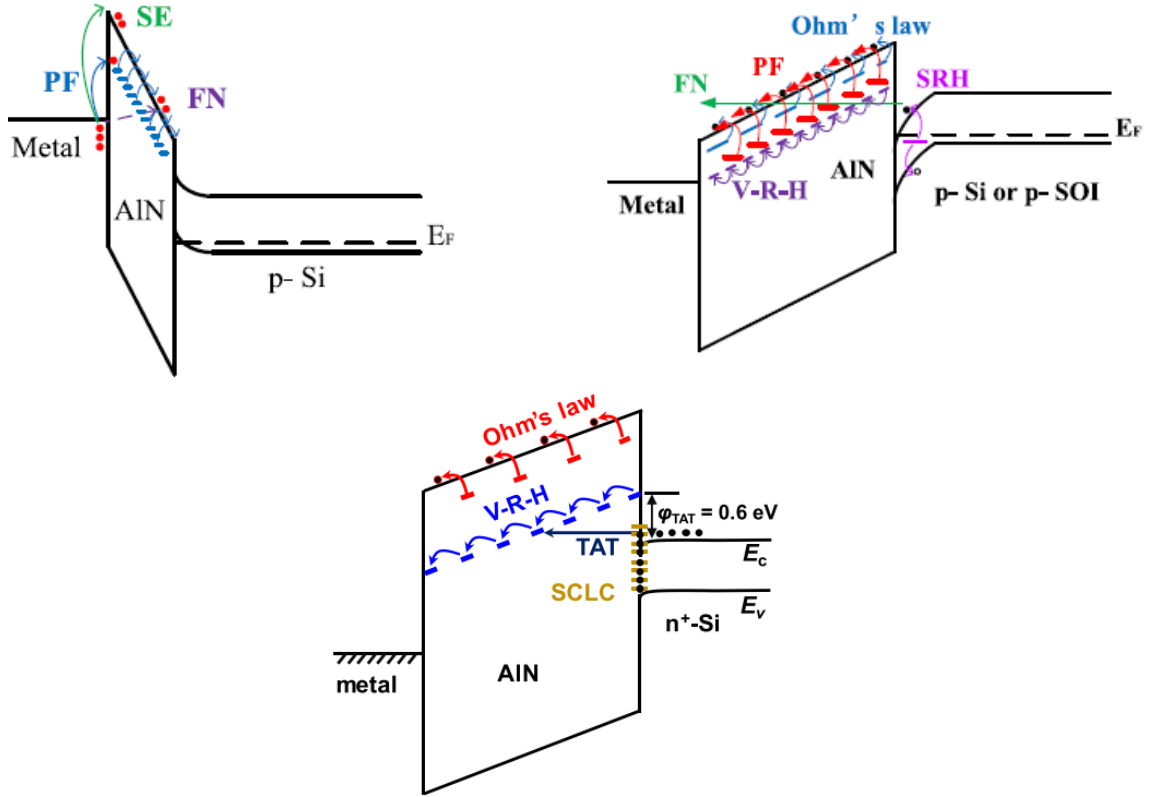
| Sample   | Current at -0.6V<br>(mA/cm <sup>2</sup> ) | Current at 0.6V<br>(mA/cm <sup>2</sup> ) | Ratio<br>(/) |
|----------|-------------------------------------------|------------------------------------------|--------------|
| NiO 5nm  | -1.88                                     | 0.43                                     | 4.20         |
| NiO 10nm | -3.20                                     | 1.29                                     | 2.47         |
| NiO 15nm | -3.77                                     | 1.12                                     | 3.40         |

**Table 14:** Summary of the absolute current ratio between -0.6 and 0.6V for the NiO samples.

Table 14 shows different leakage mechanisms at work with their representation in Figure 4.27. To determine them, the graph is modified to spot the different dependence cited in Table 15. The ones that did not show a dependence can be found in the appendices.

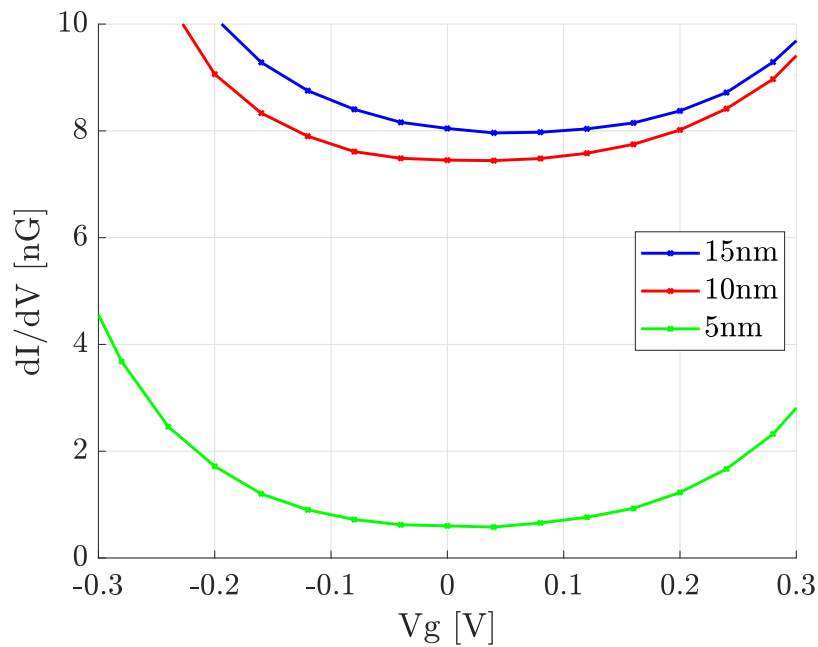
| Mechanism                               | Expression                                                                                                        | E-Field<br>dependence                               | Temperature<br>dependence                        |
|-----------------------------------------|-------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|--------------------------------------------------|
| Ohm's law                               | $J = n_0 q \mu E$                                                                                                 | $J \propto E$                                       | Yes                                              |
| Poole-Frenkel (PF)                      | $J \propto E \cdot \exp\left(\frac{\beta_{PF} E^{1/2}}{2k_B T}\right)$                                            | $\ln\left(\frac{J}{E}\right) \propto E^{1/2}$       | $\ln(J) \propto \frac{1}{T}$                     |
| Trap-assisted<br>tunneling (TAT)        | $J \sim \exp\left(-\frac{4\sqrt{2m^*}(q\varphi_B)^{3/2}}{3q\hbar E}\right)$                                       | $\ln(J) \propto \frac{1}{E}$                        | Yes                                              |
| Variable-range<br>-hopping (VRH)        | $J \sim \exp\left(\left(\frac{T_0}{T}\right)^{1/4}\right)$                                                        | $\ln(J) \propto E$                                  | $\ln(J) \propto -\left(\frac{1}{T}\right)^{1/4}$ |
| Space-charge<br>limited conduction      | $J = \frac{\varepsilon \varepsilon_0 \mu E^2}{L^3}$                                                               | $J \propto E^2$                                     | Insensitive                                      |
| Shockley-Read<br>-Hall (SRH)            | $J = \frac{qn_i W}{\tau_p e^{(E_t - E_i)/kT} + \tau_n e^{-(E_t - E_i)/kT}}$                                       | Insensitive                                         | Yes                                              |
| Schottky or thermionic<br>emission (SE) | $J \propto T^2 \cdot \exp\left(\frac{\sqrt{qE/\pi\varepsilon}}{2k_B T}\right)$                                    | $\ln(J) \propto E^{1/2}$                            | Yes                                              |
| Fowler-Nordheim (FN)                    | $J = \left(\frac{q^3 E^2}{8\pi\hbar\Phi}\right) \cdot \exp\left(-\frac{4(2m)^{1/2}\Phi^{3/2}}{3\hbar q E}\right)$ | $\ln\left(\frac{J}{E^2}\right) \propto \frac{1}{E}$ | Insensitive                                      |

**Table 15:** Summary of the leakage considered in this work. The table is taken from [65] with addition from [66].



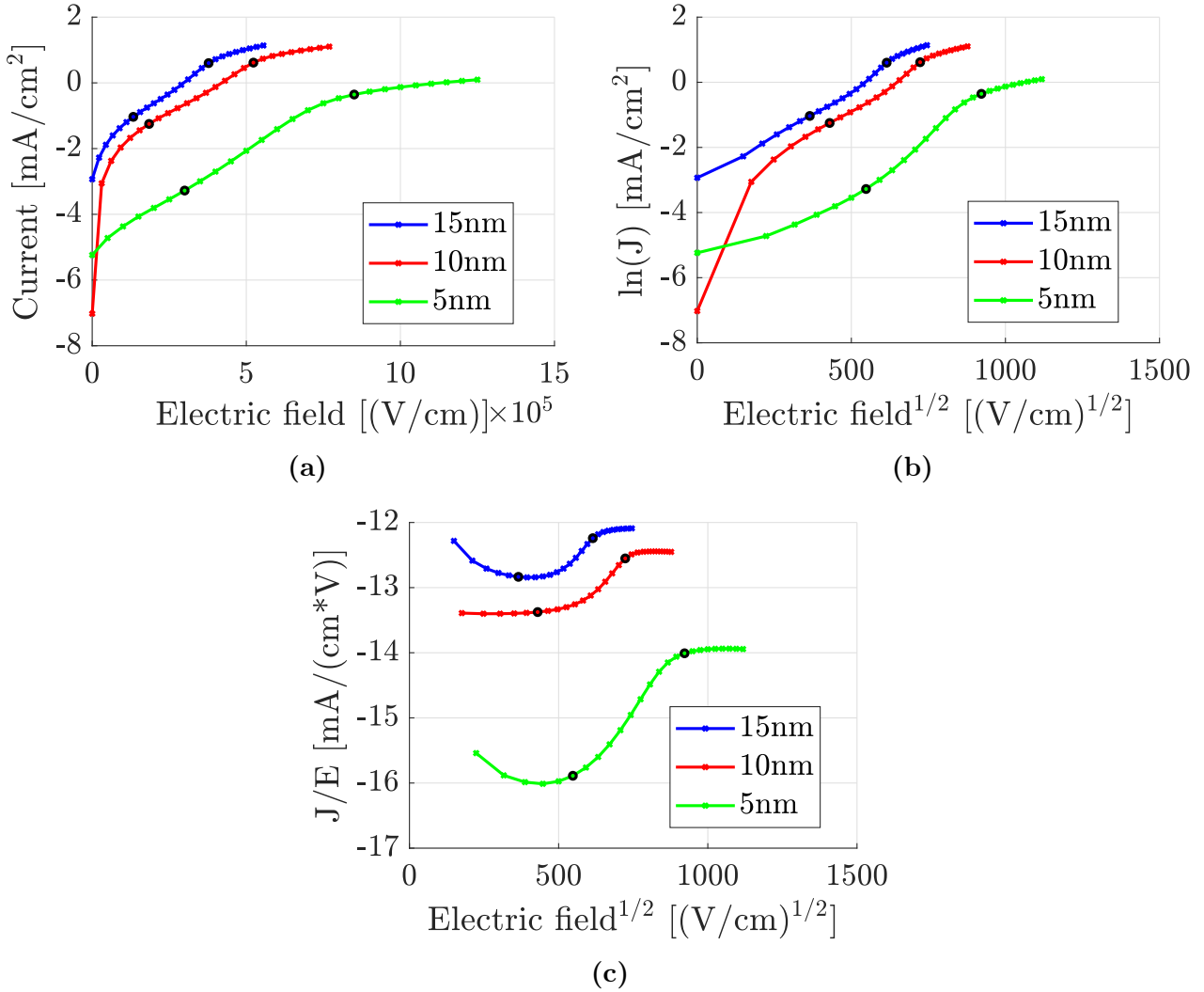
**Figure 4.27:** Representation of different leakage mechanisms. From [65], [66].

First, the low voltage zone is analysed by plotting the different derivatives of  $J$  by the voltage ( $\frac{dJ}{dV}$ ) in Figure 4.28. The plateau between -0.1 and 0.1V indicates that the Ohm's law dominates with shunt resistance of 1.66, 0.13 and 0.12 M $\Omega$  for 5, 10 and 15nm of NiO respectively. An  $R_{shunt}$  diminishing with the thickness is irregular, but can also be explicated by the creation of defects during the deposition process.



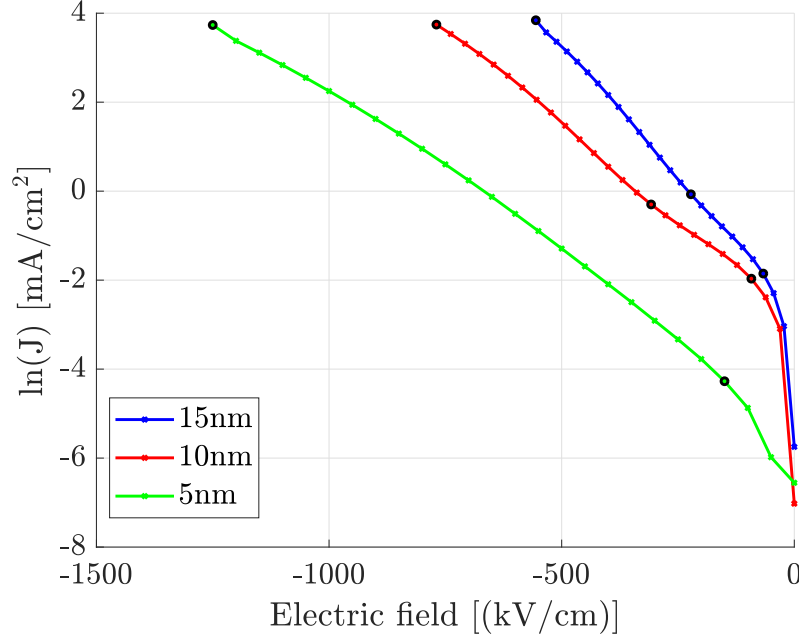
**Figure 4.28:** Derivative of the current by the voltage for the NiO samples.

For the other voltages, it is more complicated. For the end of the positive voltage, after 0.8V, the current does not seem to be influenced by the tension. Therefore, it could indicate the VRH mechanism. At middle voltage, the mechanism is, at first, considered the same. Two different mechanisms are possible, SE and VRH. Their electric field dependence are represented in Figure 4.29 a and b. If the mechanism is different for 5nm of NiO since there are fewer defects, a fourth mechanism can be considered: the Poole-Frenkel (Figure 4.29 c). To discriminate between the 4 phenomena, more measurements with a temperature variation are needed.



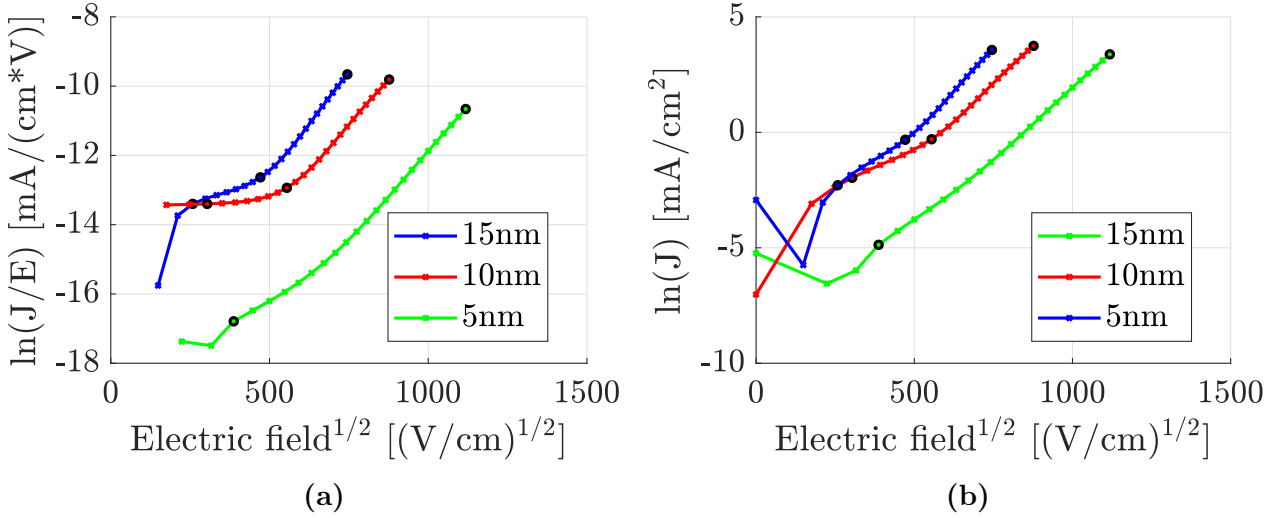
**Figure 4.29:** Electric field dependence for variable-range-hopping (VRH) (a) with the schottky emission (b) and the Poole-Frenkel (PF) (c) mechanism for the positive side of Figure 4.26. The black dots indicate the region between 0.2 to 0.7V.

Concerning the negative part, multiple solutions are also possible. In the assumption that only one mechanism is responsible for the leakage current, the variable-range-hopping (VRH) is the most likely.



**Figure 4.30:** Electric field dependence for variable-range-hopping (VRH) mechanism for the negative side of Figure 4.26. The black dots indicate the voltage at -0.1, -0.4 and -1V.

However, the 10 and 15nm sample have a slight slope change while the 5nm do not. Meanwhile, two others mechanisms can also correspond only for the NiO 5nm, the Schottky emission and the Poole-Frenkel, but not the two others thickness (see Figure 4.31). Thus, the 5nm may have only one mechanism of leakage (PF, SE or VRH).



**Figure 4.31:** Electric field dependence for Poole-Frenkel (FN)(a) and (b) mechanism for the negative side of Figure 4.26. The black dots indicate the voltage at -0.1, -0.4 and -1V.

Concerning the 10nm and 15nm, two different mechanisms may occur from -0.1 to 0.4V and from 0.4 to -1. Figures 4.30 and 4.31 already give the best candidates for the two intervals. Thus, it requires additional measurements with temperature variations to differentiate the proposed mechanisms.

#### 4.2.4 Summary

In conclusion, three different measures were performed on the different stacks to evaluate the various metrics.

The first one was the lifetime. The results showed that the silicon oxide stack ( $\text{SiO}_2(3\text{nm})/\text{Si}/\text{SiO}_2(3\text{nm})$ ) had a minority carrier lifetime of around  $46\mu\text{s}$  before annealing and was improved up to  $62\mu\text{s}$  after it, at an injection level of  $5 \times 10^{15}$ . It gave a surface recombination rate (SRV) of  $290\text{cm/s}$ . It was within range compared to literature ( $10\text{-}400\text{ cm/s}$ ). After depositing a metallic oxide by reactive sputtering and annealing, the value fell off to  $2\text{-}4\mu\text{s}$ , whether it was NiO or  $\text{WO}_3$  at injection level of  $5 \times 10^{14}$  (for  $\text{SiO}_2$  at this level, the result is  $234\mu\text{s}$ ). The apparitions of defects caused this sudden drop during the deposition process. After verification, it would seem that the oxygen during the reactive sputtering was ionised negatively and was attracted at high speed towards the wafer, creating defects. To decouple the oxidation from the deposition, the MLO recipe was proposed.

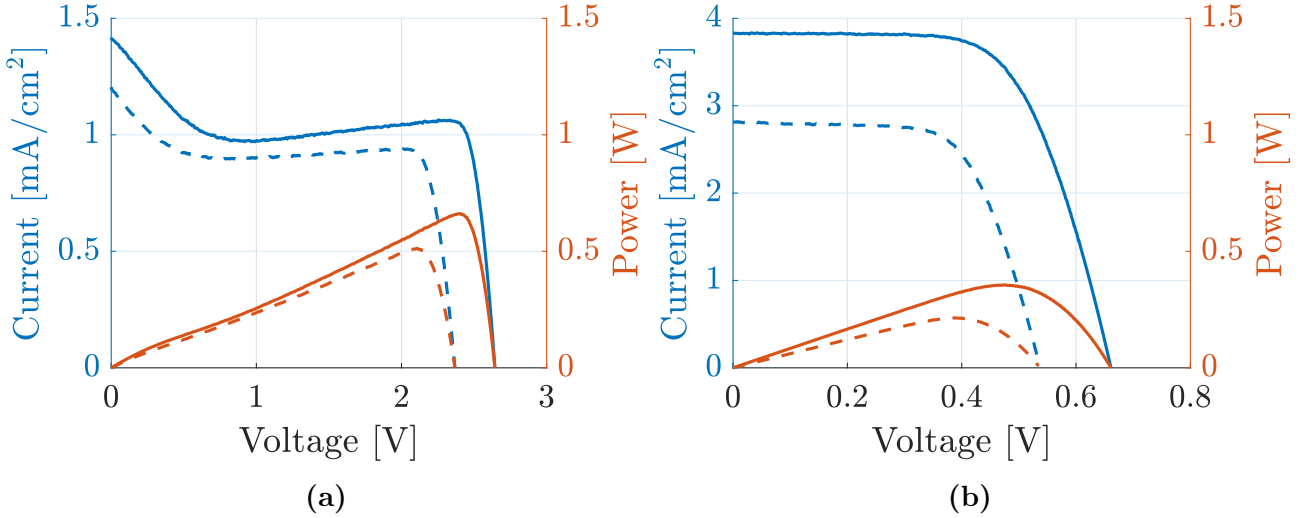
Then, CV measurements were realised. After calculating the dispersion and correcting the measures using the 6-element model for each, the flat band voltage shift was discussed. According to A. Mazurak et al. [63], it may result from the increase of majority carrier traps in the oxide. This changes  $Q_{ox}$  and thus  $V_{fb}$ . After that, the density of traps ( $D_{it}$ ) was reviewed. The measure on just the  $\text{SiO}_2$  stack already showed an higher concentration ( $1.2\text{E}12\text{ cm}^{-2}\text{eV}^{-1}$ ) compare to what was found in the literature ( $1\text{-}10\text{E}11\text{ cm}^{-2}\text{eV}^{-1}$ ). Concerning the metal oxide, the thickness impact for NiO appeared to decrease the  $D_{it}$  for an unknown reason (to  $2.2$  to  $1.56\text{E}12\text{ cm}^{-2}\text{eV}^{-1}$ ). While the impact of annealing clearly reduced the interface trap density ( $1.88\text{E}12$  to  $8.4\text{E}11\text{ cm}^{-2}\text{eV}^{-1}$ ). The last measure done with CV was an hysteresis. It clearly showed that mobile charge are produced when the  $\text{SiO}_2$  was grown, not with the deposition. They were reduced by raising the annealing temperature. An interesting result was the sign change when the measure is done at  $1$  or  $10\text{kHz}$ . It was supposed that at  $10\text{kHz}$ , fewer defects near an interface were probed and the dominant mechanism differed from the one at  $1\text{kHz}$ .

Lastly, the conduction mechanisms were analysed with IV measurements. Multiple were proposed, like the variable-range-hopping or the Poole-Frenkel, that dominates at a different voltage. More measurements with temperature variations are needed to discriminate all of the proposed mechanisms.

## 4.3 PV Cell under radiation

### 4.3.1 Light IV

On the 3 different cells, only two were measured under an AM1.5 calibrated light: the silicon and the triple-junction. The setup was not adapted for the CIGS, resulting in a highly noisy output. Thus, Figure 4.32 and Table 16 presents the results before and after radiation.

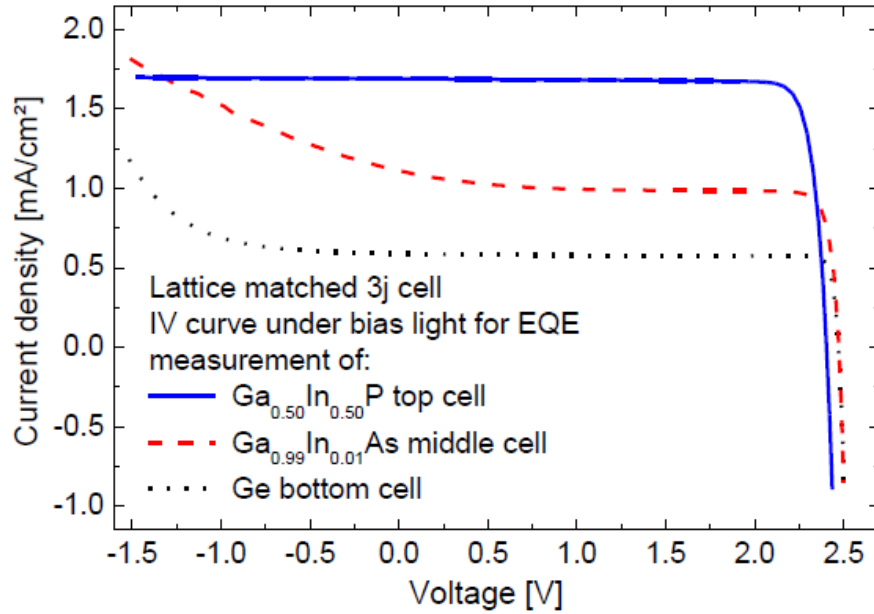


**Figure 4.32:** IV measurements under an AM1.5 calibrated light for the triple-junction (a) and the silicon (b) solar cell. The left blue side is the current density and the orange right side is the generated power. The solid lines are before radiation and the dashed lines are after radiation.

|                | Triple-junction |          |           | Silicon |          |           |
|----------------|-----------------|----------|-----------|---------|----------|-----------|
| Parameters     | Pre-rad         | Post-rad | Variation | Pre-rad | Post-rad | Variation |
| $I_{sc}$ [A]   | 0,36            | 0,31     | -14,4%    | 0,83    | 0,61     | -26,5%    |
| $V_{oc}$ [V]   | 2,64            | 2,36     | -10,5%    | 0,66    | 0,53     | -18,7%    |
| FF [%]         | 66,82           | 68,89    | +2,0%     | 64,5    | 65,0     | +0,5%     |
| Efficiency [%] | 24,63           | 19,45    | -5,1%     | 16,3    | 9,83     | -6,5%     |

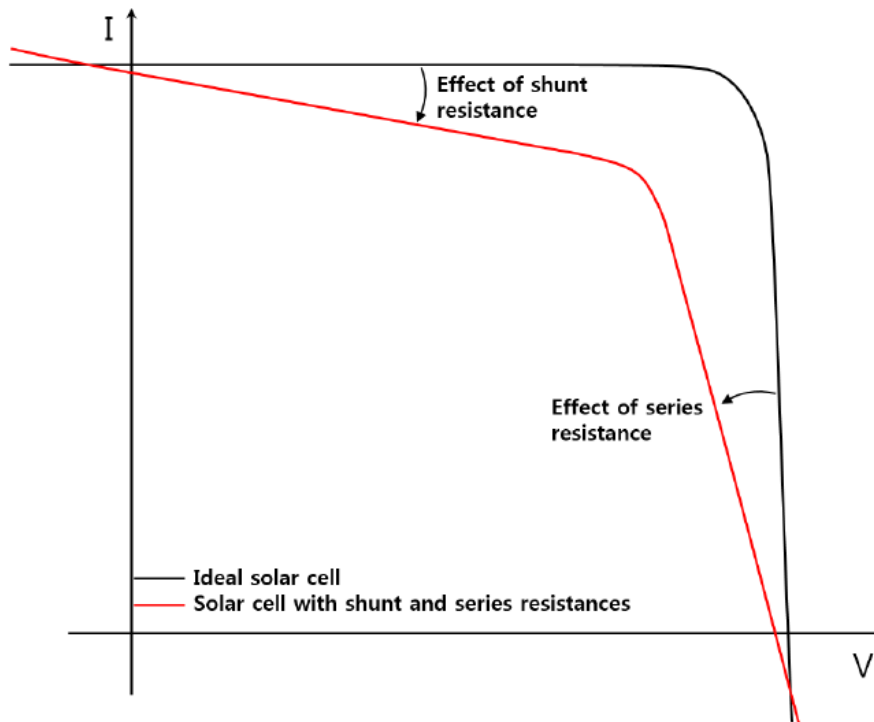
**Table 16:** Summary of the different important parameters extracted for the triple-junction and the silicon solar cell.

The first noticeable trend is the different evolution of the current. The silicon trend is expected for all solar cells, but the triple-junction goes down suddenly to climb back a little afterwards. It is due to the lighting condition. Indeed, the cell is calibrated to work in space, where the light spectrum is different from the one reaching the ground. More precisely, the spectrum to analysed this solar cell should be AM0 but the only one available in Welcome's lab is the AM1.5. Thus, on the triple junction, only 1 or 2 produced current (the middle and/or the last one), limiting the maximum. Figure 4.33 presents the different possible cases.



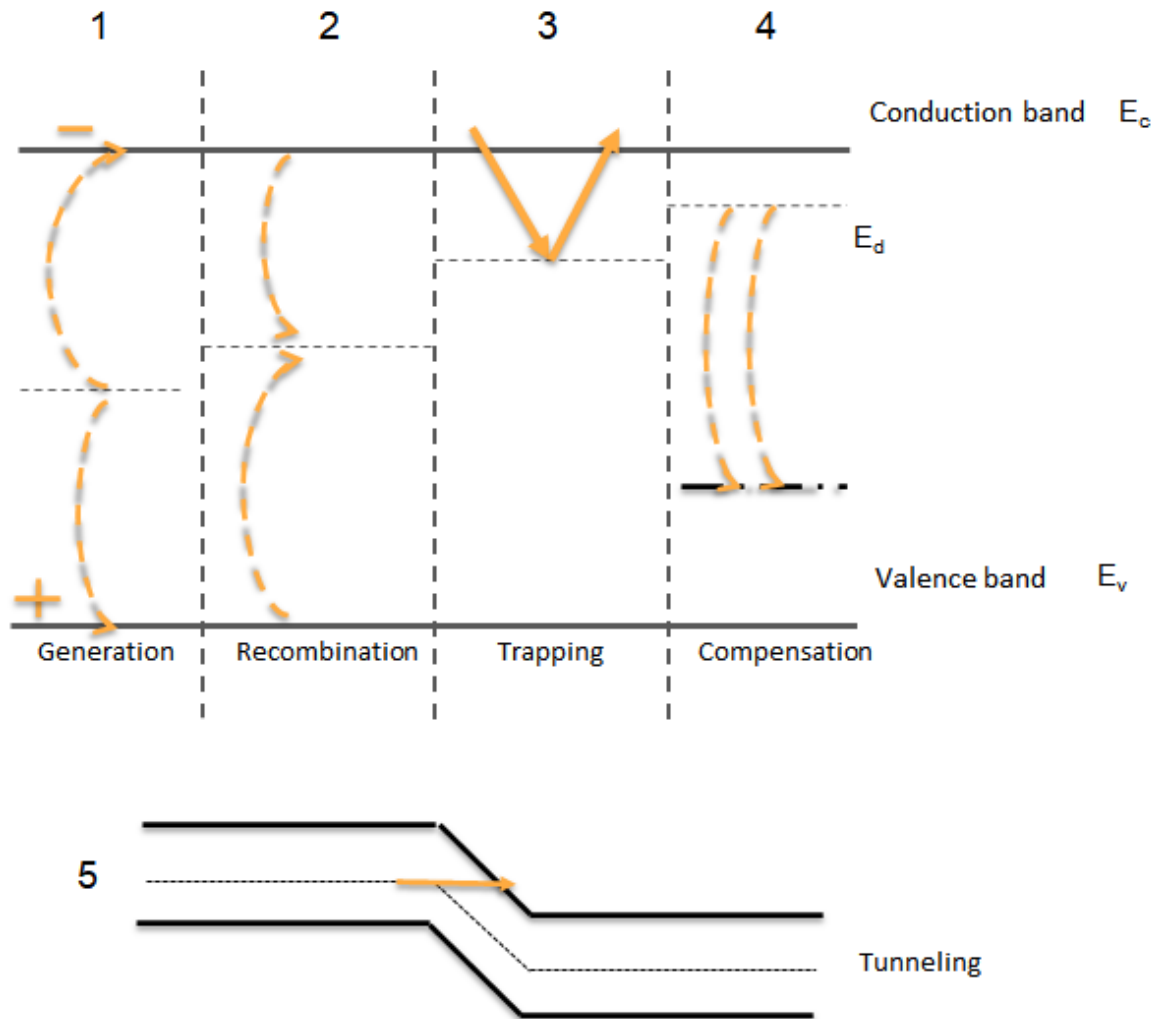
**Figure 4.33:** I-V-curves taken from a triple-junction cell while different bias light conditions. From [67].

The second analysis to draw is the relative no impact of the radiation on the filling factor (FF) on both solar cells. It means that the series resistance and the shunt resistance are not too much impacted (see Figure 4.34). Thus, the damages are mostly done in the absorption layers and not at the interfaces, the opposite of the CIGS cell (that will be discussed later).



**Figure 4.34:** Effect of series and shunt resistances on the filling factor. From [68].

Finally, The different variations/degradations (more important for the silicon solar cell) are consistent with the literature.  $I_{sc}$  is reduced by  $\approx 15\%$  and  $\approx 20\%$  for the triple-junction and the silicon, respectively [69]–[71]. The different degradations come from displacement damage due to the protons radiation. It moves the atoms from their equilibrium position, causing defects, like vacancies, to form recombination centres (2 in Figure 4.35). This decreases the diffusion length of minority carriers, diminishing the  $I_{sc}$ . For the  $V_{oc}$ , the defects also generate more free charge carriers. These charges are then brushed away by the electric field, producing a current and increasing the forward bias that degrades the open-circuit voltage. Other mechanisms coming from the created defects, deteriorate the cell. Like trapping, compensation and reduction of the tunnelling potential (3 to 5 in Figure 4.35).



**Figure 4.35:** Effects of the radiation on the energies bands. Adapted from [72].

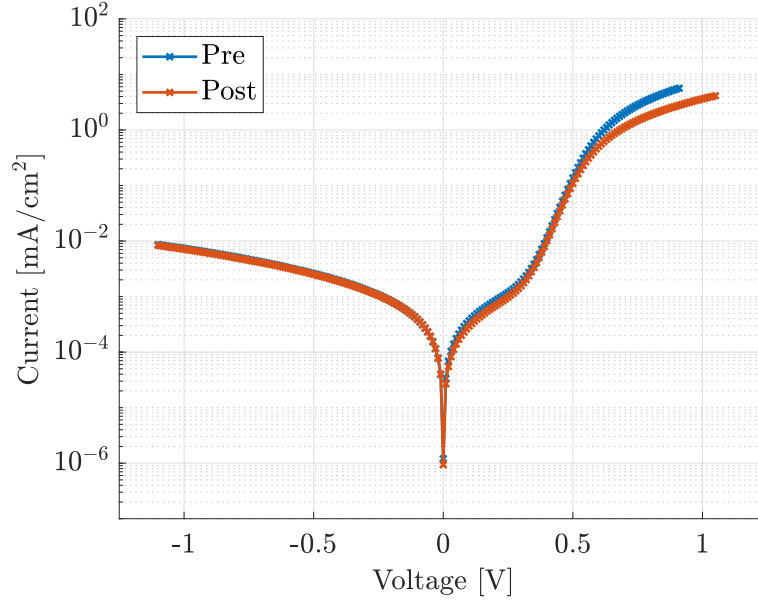


### 4.3.2 Dark IV

Due to the quantity of information, this section will be divided between the 3 solar cells.

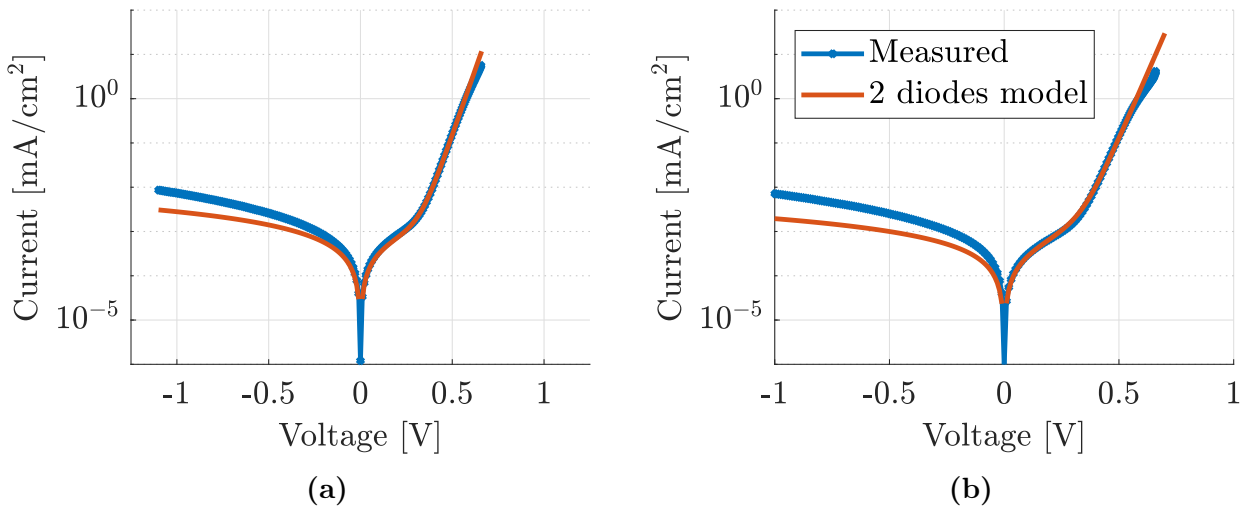
#### CIGS

Figure 4.36 presents the raw measurements before and after radiations for the best CIGS cell from the different. At first glance, it has a relatively small effect on the measures. The tendency is confirmed with the extraction of the different parameters of the 2-diodes model.



**Figure 4.36:** Current-voltage measurements of the CIGS solar cell pre and post-radiation.

Concerning the model, Figure 4.37 presents the final result of the extraction of the different parameters by plotting the corrected measures with their model. The method used is explained in the methods chapter. Table 17 summarizes the effect of radiation on the variables.



**Figure 4.37:** Comparison between the 2 diodes model and the measurement (without the series resistance) for pre-radiation (a) and post-radiation (b).

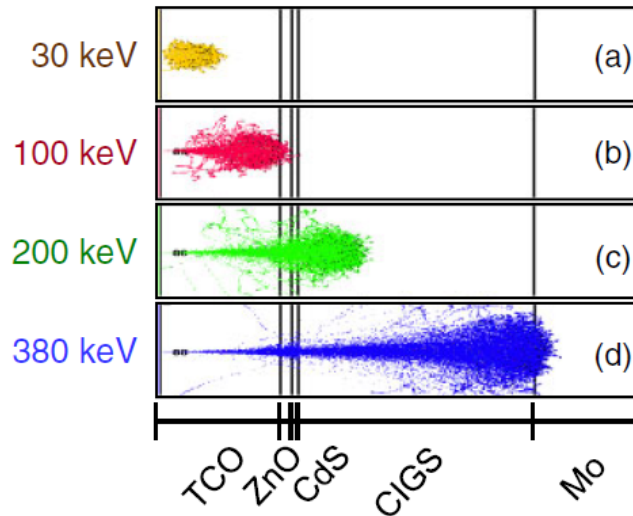
| Parameters                  | Pre-radiation | Post-radiation | Variation |
|-----------------------------|---------------|----------------|-----------|
| $R_{sh}$ [ $\Omega.cm^2$ ]  | 1.81E4        | 2.00E4         | 10.7%     |
| $R_s$ [ $\Omega.cm^2$ ]     | 3.00          | 6.32           | 110.8%    |
| $J_2$ [mA/cm <sup>2</sup> ] | 1.81E-5       | 4.68E-5        | 158.5%    |
| $n_2$ [/]                   | 3.75          | 4.06           | 8.5%      |
| $J_1$ [mA/cm <sup>2</sup> ] | 1.72E-7       | 1.34E-7        | -22.4%    |
| $n_1$ [/]                   | 1.41          | 1.41           | 0%        |

**Table 17:** Summary of the different parameters of the 2 diodes model extracted for the CIGS solar cell.

As explained in the methods chapter, the difference in reverse bias can be attributed either to an overestimation of  $R_{sh}/J_2$  or a loss mechanism not taken into account in the model. Thus, the variation of the shunt resistance is not important enough to conclude to an increase.

Concerning the variations of the parameters, the current density due to generation/recombination,  $J_2$ , and the series resistance,  $R_s$  are the only ones having a considerable increase. The first one indicates that the same mechanism, described in the previous section, is also at play. The radiation creates recombination centres. If the cell had been measured under a calibrated light, the short-circuit current,  $I_{sc}$  would certainly have been lowered. As for  $R_s$ , the back contact in molybdenum is deteriorated by the radiation raising its resistance.

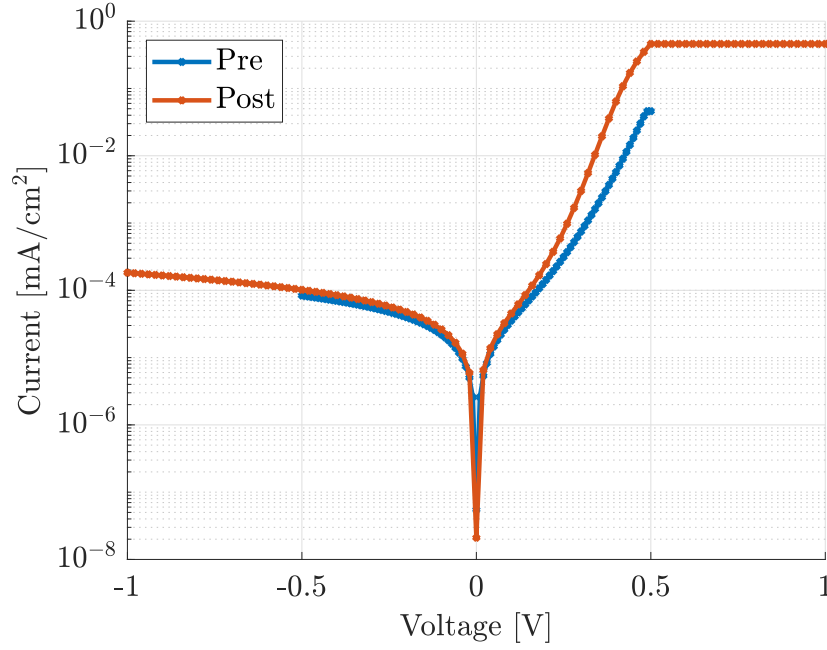
In order to demonstrate why only these two parameters worsen, compared two the two other cells, one has to watch the path taken by the protons in function of its energy (see Figure 4.38). Since the energy of the protons during the radiation are set at 10 Mev (nearly 30 times higher than the one simulated) and the fact that it is an ultra-thin solar cell, it suggests that the protons pass through the whole cell resulting in minimal damage. Arriving at the back contact, it is more sensitive to the radiation and that is the reason why in Figure 4.37, only the series resistance seems to be impacted.



**Figure 4.38:** Proton tracks in CIGS solar cells at (a) 30, (b) 100, (c) 200, and (d) 380 keV proton energy, determined by SRIM simulation. From [73].

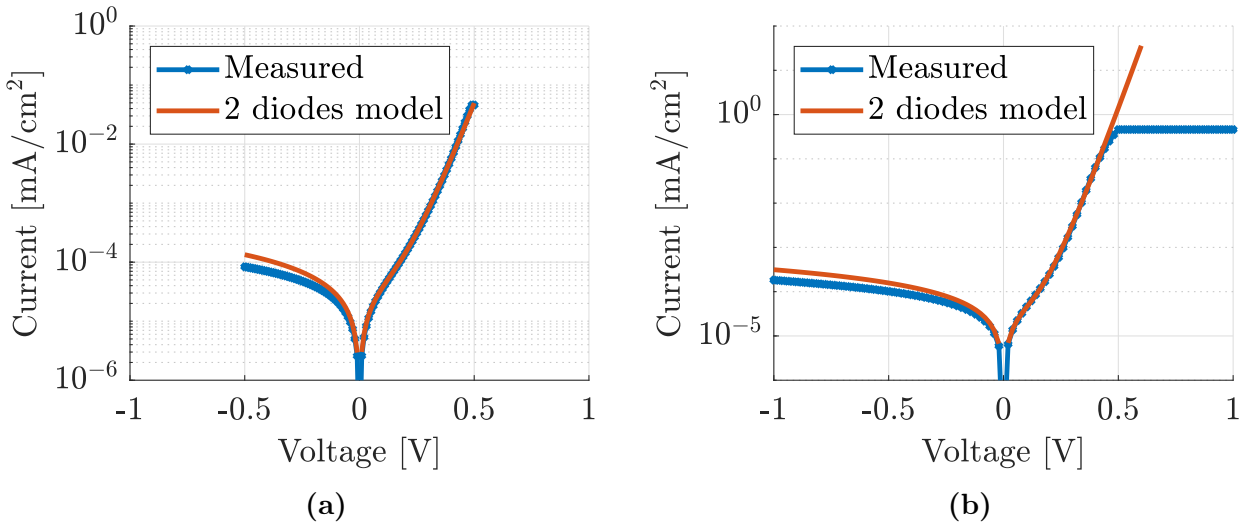
## Silicon

Concerning the silicon solar cell, the raw measurements are presented in Figure 4.39. Firstly, due to a manipulation error, the compliance was set a decade too low for the pre-radiation. That is the reason why the measure is between -0.5 to 0.5V. Secondly, the problem was fixed for the second measure. But, unfortunately, it still reaches the maximum compliance of the measurement device (0.1A). As a consequence, the series resistance cannot be extracted.



**Figure 4.39:** Current-voltage measurements of the silicon solar cell pre and post-radiation.

As for the models presented in Figure 4.40, it overestimates the reverse bias region. It shows the difficulty to differentiate the impact of the shunt resistance and the second diode. The different parameters are presented in Table 18.



**Figure 4.40:** Comparison between the 2 diodes model and the measurement for pre-radiation (a) and post-radiation (b).

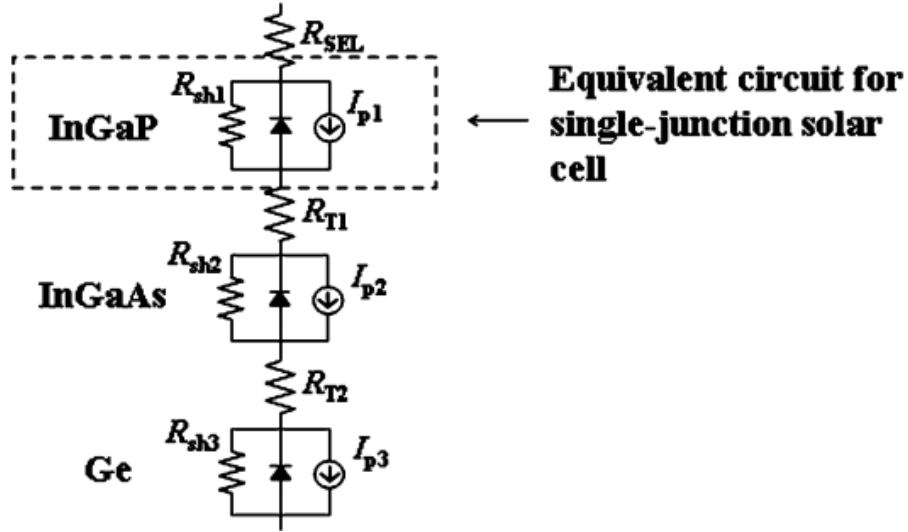
| Parameters                 | Pre-radiation | Post-radiation | Variation |
|----------------------------|---------------|----------------|-----------|
| $R_{sh}$ [ $\Omega.cm^2$ ] | 1.77E4        | 1.47E4         | -17.2%    |
| $R_s$ [ $\Omega.cm^2$ ]    | /             | /              | /         |
| $J_2$ [ $mA/cm^2$ ]        | 1.64E-6       | 1.05E-6        | -36.1%    |
| $n_2$ [/]                  | 1.94          | 1.56           | -19.24%   |
| $J_1$ [ $mA/cm^2$ ]        | 1.10E-8       | 6.31E-8        | 475.3%    |
| $n_1$ [/]                  | 1.37          | 1.16           | -15.9%    |

**Table 18:** Summary of the different parameters of the 2 diodes model extracted for the silicon solar cell.

Nearly all different variations are expected and are still caused by the defects created by the radiation. The substantial rise of the current density,  $J_1$ , is concordant with the literature [71]. This, alongside with the improved ideality factors  $n_1$ , indicates that the defects are created in the base region of the solar cell [74]. It would have been possible to link this with the penetration length of protons in silicon at 10 Mev (0.7mm). But unfortunately, there is no datasheet detailing the structure of the solar cell.

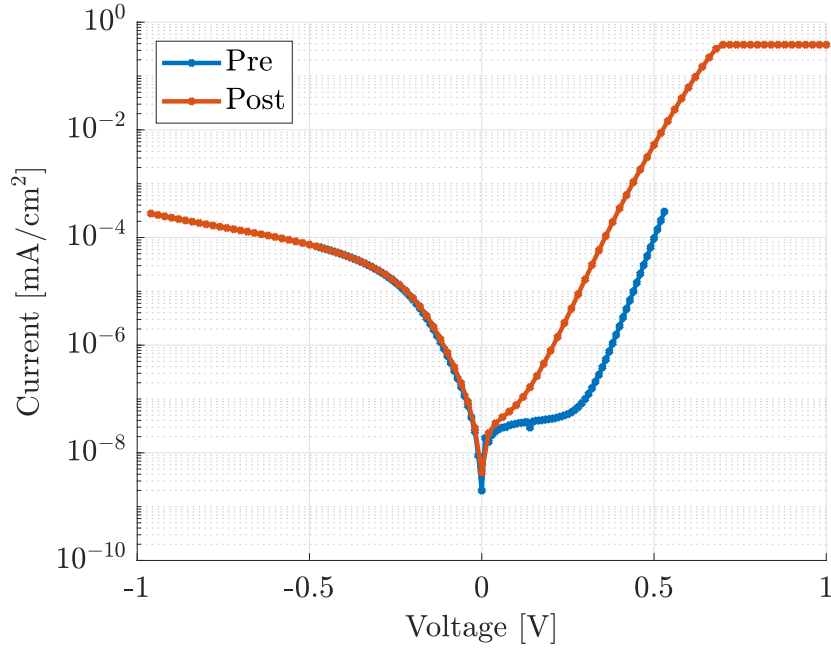
### Triple-junction

For the triple-junction, it is not possible to apply the two-diodes model since it is basically 3 different solar cells stack on each other. The correct model is shown in Figure 4.41. Thus, a simpler analysis with just one diode is made to extract the ideality factor and the shunt resistance of the whole structure.



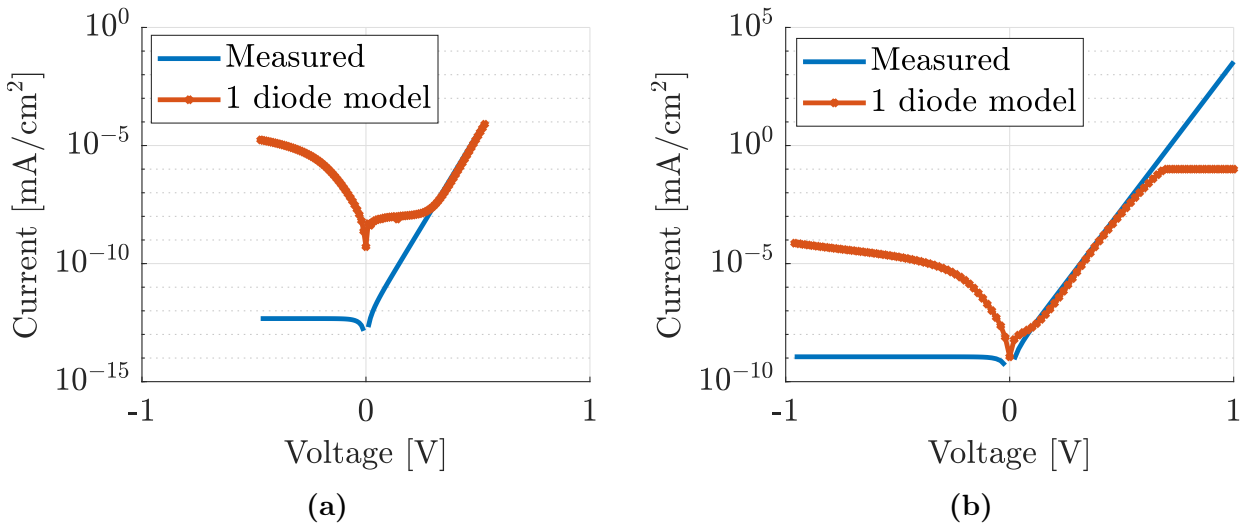
**Figure 4.41:** Schematic of the equivalent circuit model for the triple-junction solar cell; the dotted frame shows the equivalent circuit model for a single-junction solar cell. From [75].

The same mistake on the compliance was made during the measurement (see Figure 4.42) of this cell. This is the reason why the first measure goes only from -0.5 to 0.5V. Unfortunately, the maximum compliance is also reached for the post-radiation measurement. Thus, the series resistance cannot be extracted.



**Figure 4.42:** Current-voltage measurements of the triple-junction cell pre and post-radiation.

The 1 diode model fit is presented in Figure 4.43 with the extracted parameters summary in Table 19.



**Figure 4.43:** Comparison between the 1 diode model and the measurement for pre-radiation (a) and post-radiation (b).

| Parameters                 | Pre-radiation | Post-radiation | Variation |
|----------------------------|---------------|----------------|-----------|
| $R_{sh}$ [ $\Omega.cm^2$ ] | 3.33E6        | 2.77E6         | -26.9%    |
| $R_s$ [ $\Omega.cm^2$ ]    | /             | /              | /         |
| $J_1$ [ $mA/cm^2$ ]        | 1.79E-7       | 4.31E-4        | 241E3 %   |
| $n_1$ [/]                  | 1.03          | 1.33           | 29.1%     |

**Table 19:** Summary of the different parameters of the 1 diodes model extracted for the triple junction solar cell.

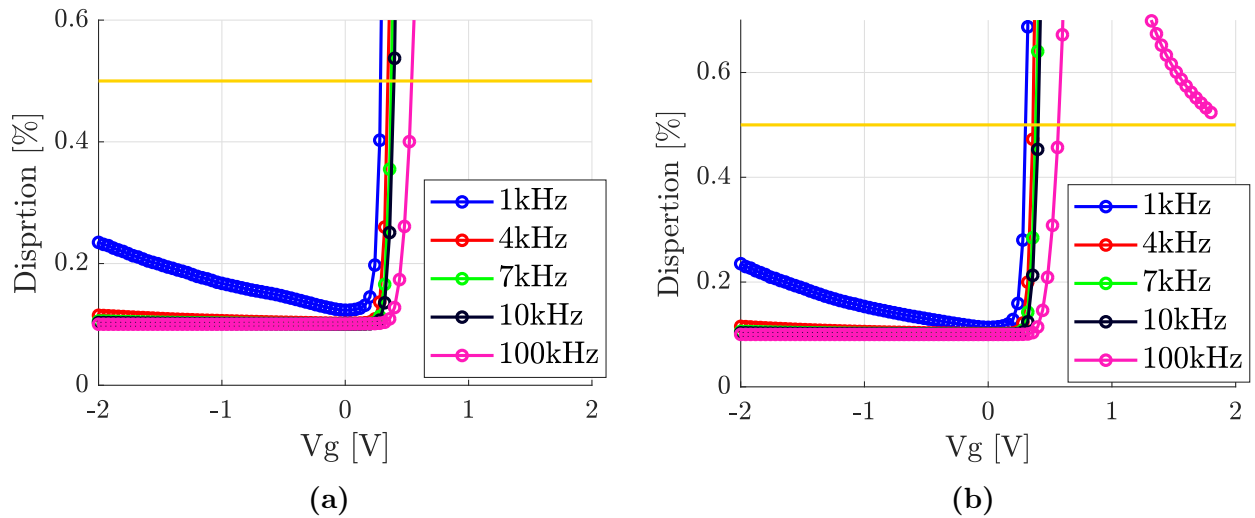
The enormous change in the current density comes from the model used and translates a threshold voltage change. S. Park et al. [76] have investigated this change. They found that came from an excess current in the last junction (Ge cell) which impacted the whole dark IV curve. After a thermal analysis, they concluded that the excess was due to band to band tunnelling. Thus, when the cells are irradiated, defects are created and the tunnelling is easier: the charge carrier goes through a defect state before decaying to the other band on the other side of the junction.

### 4.3.3 Dark CV

Concerning the CV measurements, the 3 solar cells were measured, but only 2 are analyzed in this work. Indeed, the triple-junction is too complex to analyse since it is basically 3 devices linked to each other. However, it is possible to measure them individually to analyse their degradation after radiation. But to do so, the triple-junction has to be illuminated with light sources which energy is near one of the subcell bandgaps [77]. Due to the quantity of information, this section will be divided between the 2 solar cells (CIGS and silicon).

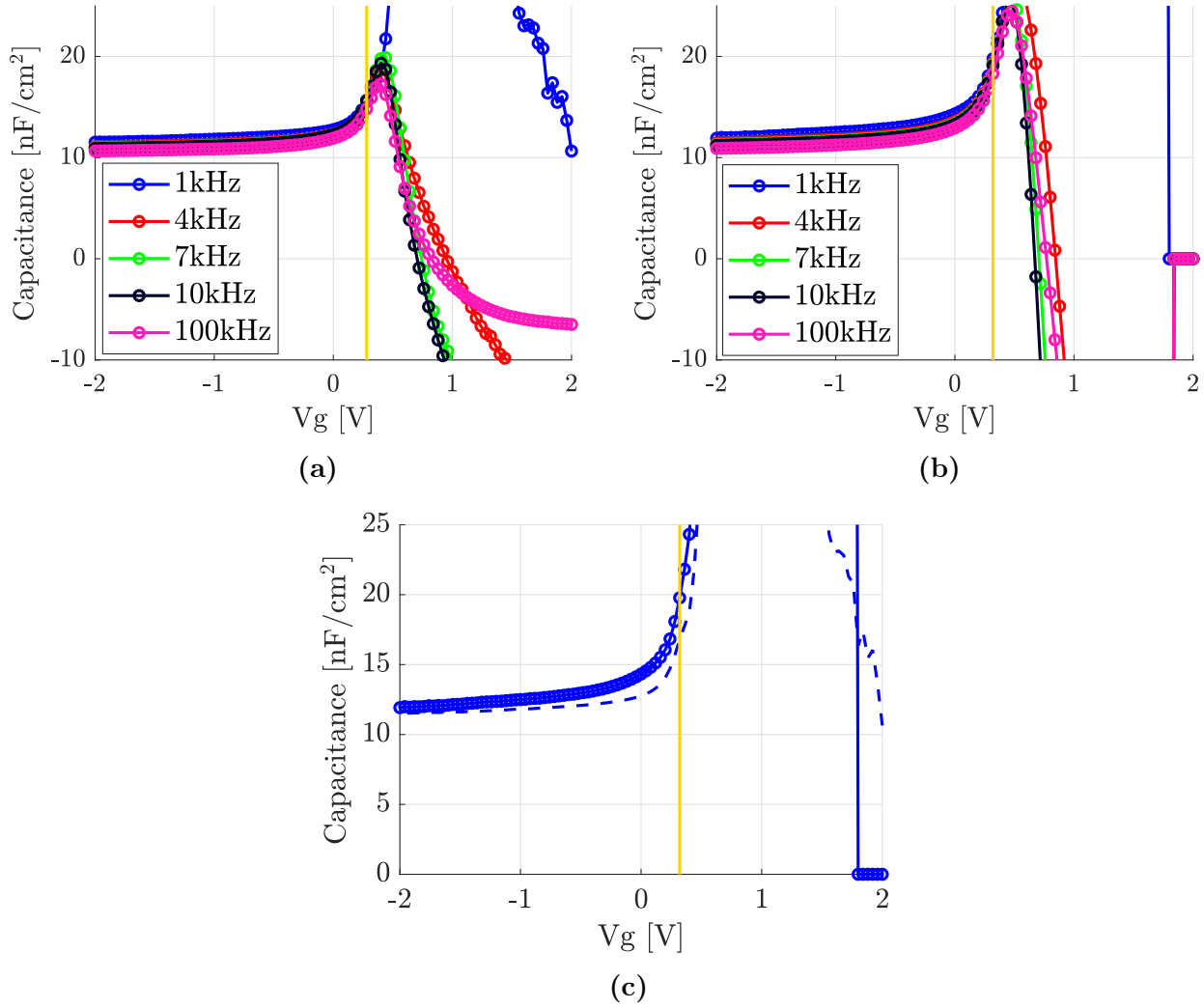
### CIGS

Only one cell of the 4 measured after radiation gives interpretable curves to analyse. Thus only one is treated. The same procedure used for the CV measurements of the NiO and WO<sub>3</sub> is applied. First, the dispersion before and after the radiation is plotted in Figure 4.44 to assess the measure. It shows that after 0.28V, the measure cannot be trusted. It makes sense because, at this voltage, the PN junction starts to conduct electricity, raising the conduction and the dispersion factor.



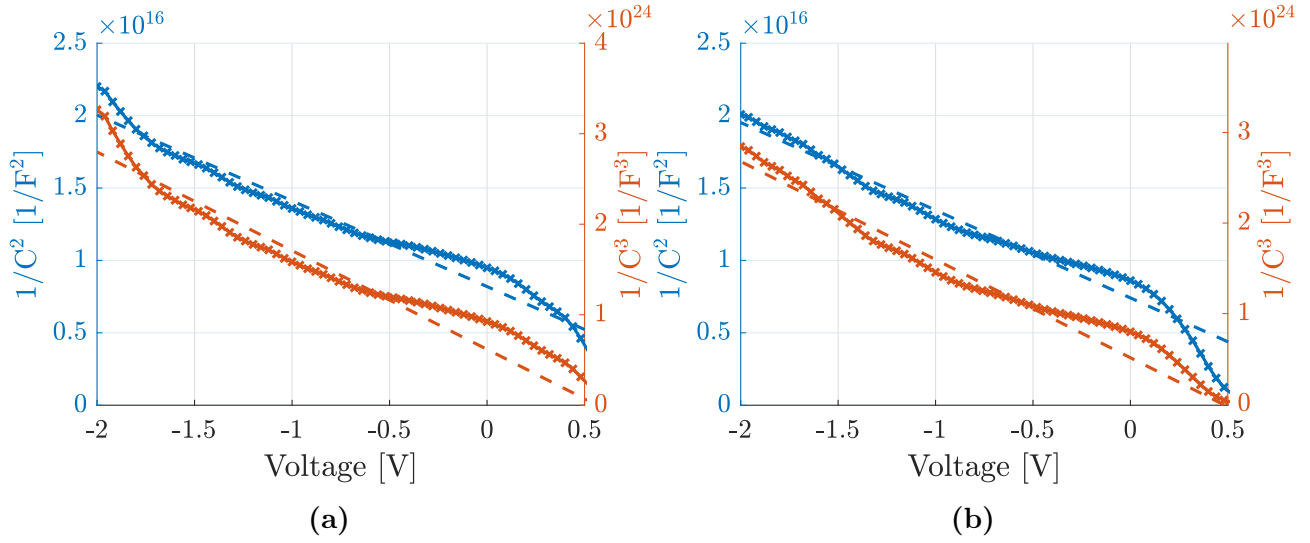
**Figure 4.44:** Dispersion factor versus the voltage for the CIGS solar cell for pre-radiation (a) and post-radiation (b). The yellow line is when  $D=0.5\%$ .

Figure 4.45 presents the measure pre and post-radiation. After 0.28V (the yellow line), the trend is incoherent and even goes in the negative. The reason is that the device cannot make the difference between the conduction and the capacitance. The measures are not corrected because it varies slightly (less than  $\pm 0.5$  nF/cm<sup>2</sup>). For the pre-radiation, the values and tendencies are nearly identical to other measurements on the same type of cell performed by Welcome's lab. Concerning the variation before and after radiations, the capacitance rises a little.



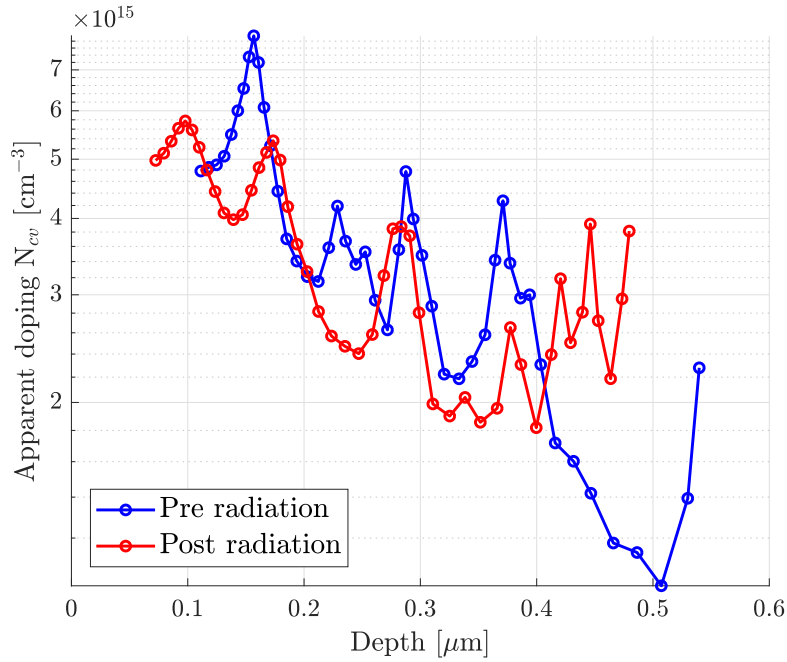
**Figure 4.45:** CV measurements for the CIGS solar cell for pre-radiation (a) and post-radiation (b). Figure C compares the two graphs with the result at 1kHz (the dashed lines are pre-radiations). On the right of the yellow line, the dispersion is greater than 0.5%.

Concerning the apparent doping extraction, Figure 4.46 shows the  $1/C^2$  and  $1/C^3$  plots. The curves are not evolving as expected since none are quite linear. Nevertheless, the most linear is the  $1/C^2$  for both with an  $R^2$  of 0.97 and 0.96 for the pre and post-radiation, respectively. While the  $1/C^3$  are at 0.93 and 0.95. The build-in voltage goes from 1.38 to 1.22 which seems rather high.



**Figure 4.46:** Plot of  $1/C^2$  and  $1/C^3$  versus the voltage for a silicon solar cell for pre-radiation (a) and post-radiation (b). The dashed lines are the linear regression.

Finally, Figure 4.47 presents the extracted apparent doping versus the depth. The values for the pre-radiation concord with previous measurements not yet published. Concerning the effect of radiations, the detected defects seem to be localised after 400nm, near the end of the cell. The results agreed with the simulation and result presented in the light IV. However, more measurements are needed to confirm the outcomes since Figure 4.45 is unusual.

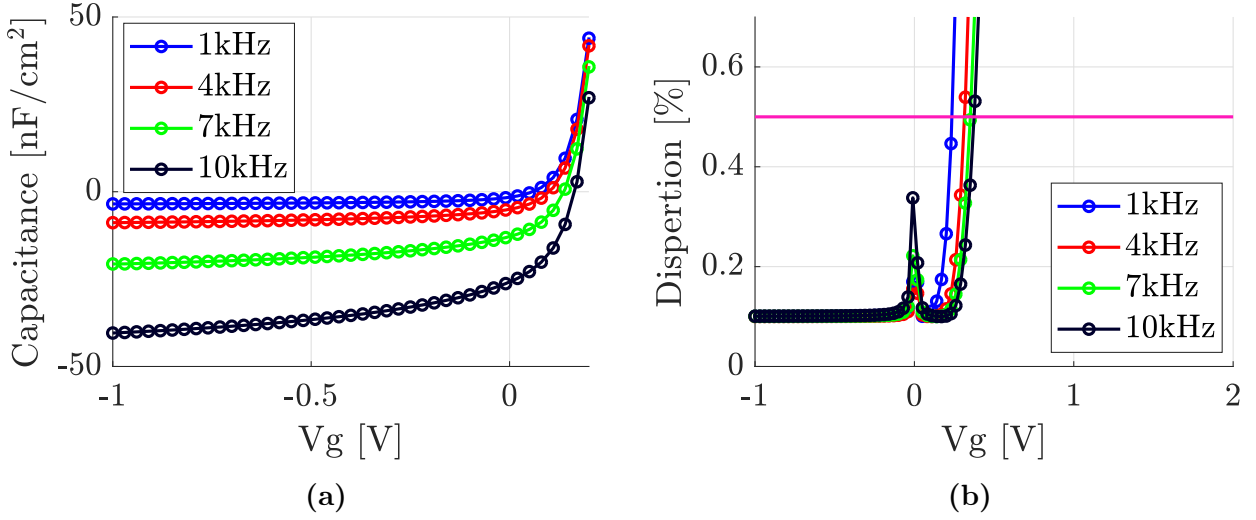


**Figure 4.47:** Apparent doping concentration versus the depth for the CIGS solar cell pre and post-radiation.



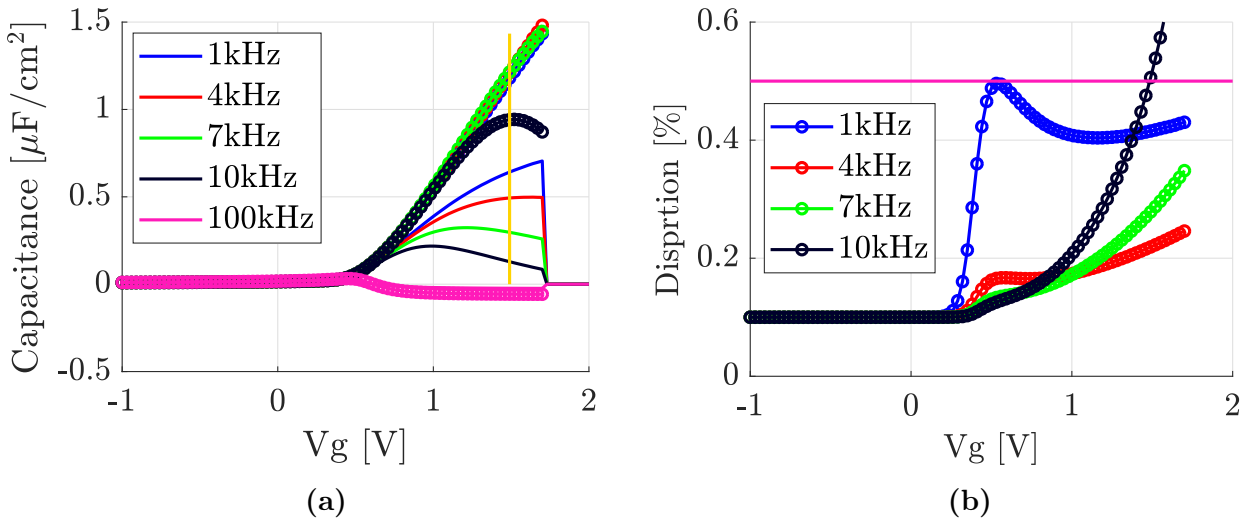
## Silicon

For the silicon solar cell, the junction after radiation is too damaged to have a correct measure, even though the dispersion is correct. The measure gives a negative capacitance for nearly all points (see Figure 4.48). Thus, only the pre-radiation measures are analysed.



**Figure 4.48:** CV measurements (a) and dispersion (b) for the silicon solar cell post-radiation.

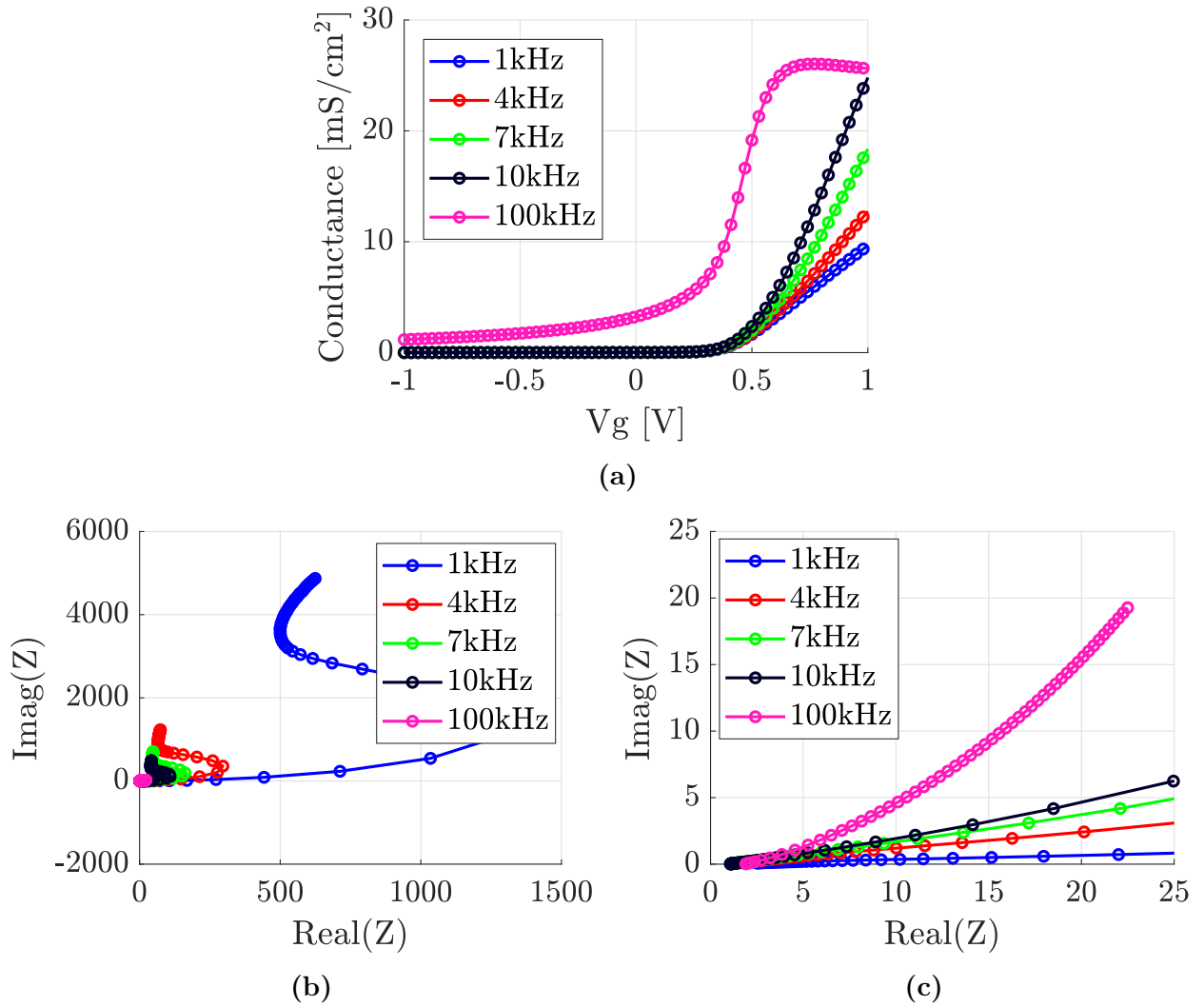
These measures are presented in Figure 4.49 with the correction that removes the effect of the frequency. The obtained series resistance is  $0.75\Omega$ . As for the dispersion, it is under 0.5% for nearly all frequencies except the 10kHz after 1.5V. It may explain the difference with the other curves around this voltage. The 100kHz has a different behaviour and is not shown in the dispersion. It will be discussed hereafter.



**Figure 4.49:** CV measurements with the correction (the marked lines) (a) and dispersion (b) for the silicon solar cell pre-radiation. On the right of the pink line, the dispersion is greater than 0.5%

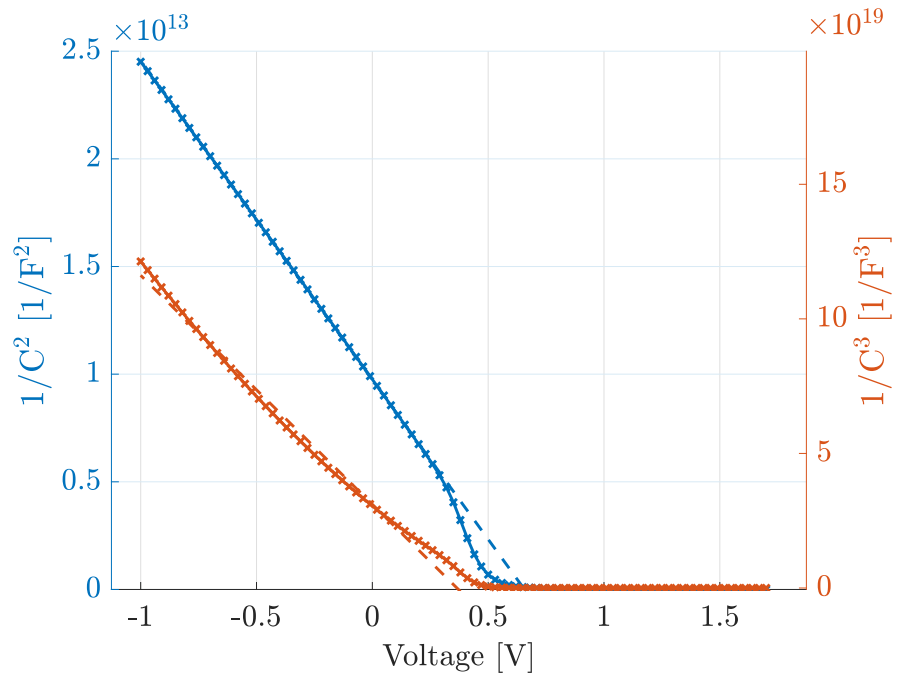
About the 100kHz, Figure 4.50a presents the conductance versus the voltage. The trend of the 100kHz is also different and above the others frequencies and is thus frequency dependent. To investigate it, the Nyquist plot, with a zoom, is shown in Figure 4.50b and c. It highlights the change of behaviour after 10Khz and that imaginary part seems equals to the real part for the 100kHz curve.

Knowing this and that the conductance starts to be frequency dependent, it can indicate that the quasi-static limit is exceeded. The condition to have a quasi-static measure is  $\omega\tau < 1$  (with  $\omega$  the angular frequency and  $\tau$  the minority carrier lifetime). If the limit is exceeded after 100kHz and not 10kHz, the lifetime of the solar cell is roughly between  $1.6\mu s$  and  $16\mu s$  ( $= \tau = \frac{1}{\omega}$ ). It is in the low range of what is found in the literature ( $5$  to  $500\mu s$ ) [78].

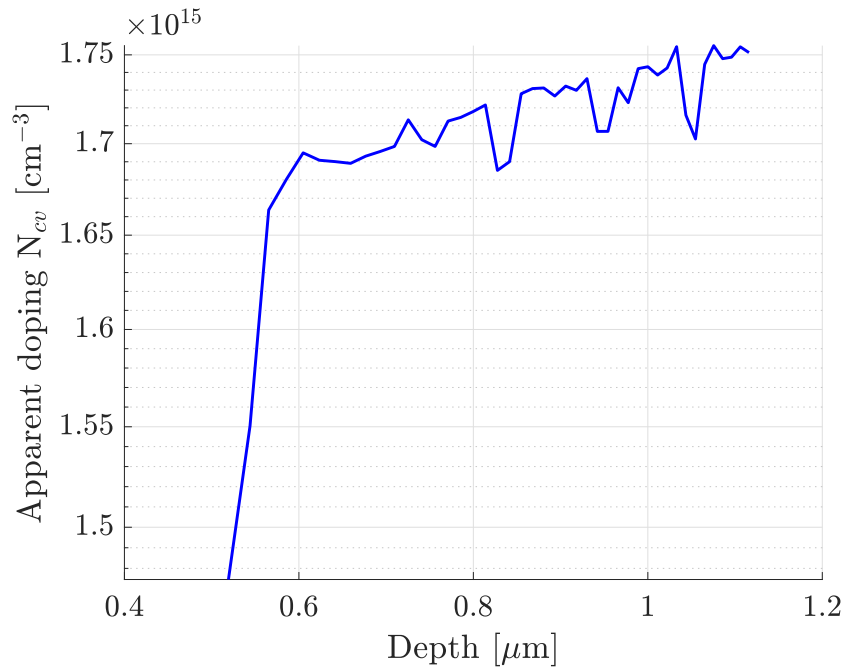


**Figure 4.50:** Conductance versus the voltage (not corrected) (a) with also the Nyquist plot (b) with a zoom (c) for the silicon solar cell.

As for the extraction of the apparent doping, the  $1/C^2$  and  $1/C^3$  are presented in Figure 4.51. The linearity is better with the  $1/C^2$ . Thus, it confirms a uniform voltage with a built-in voltage of 0.66V. Then, the apparent doping is extracted and shows versus the depth in Figure 4.52. The values are in the lower bond of what the industry produces:  $1 \cdot 10^{15}$  to  $1 \cdot 10^{18} \text{ cm}^{-3}$  [79], [80].



**Figure 4.51:** Plot of  $1/C^2$  and  $1/C^3$  versus the voltage for a silicon solar cell. The dashed lines are the linear regression.



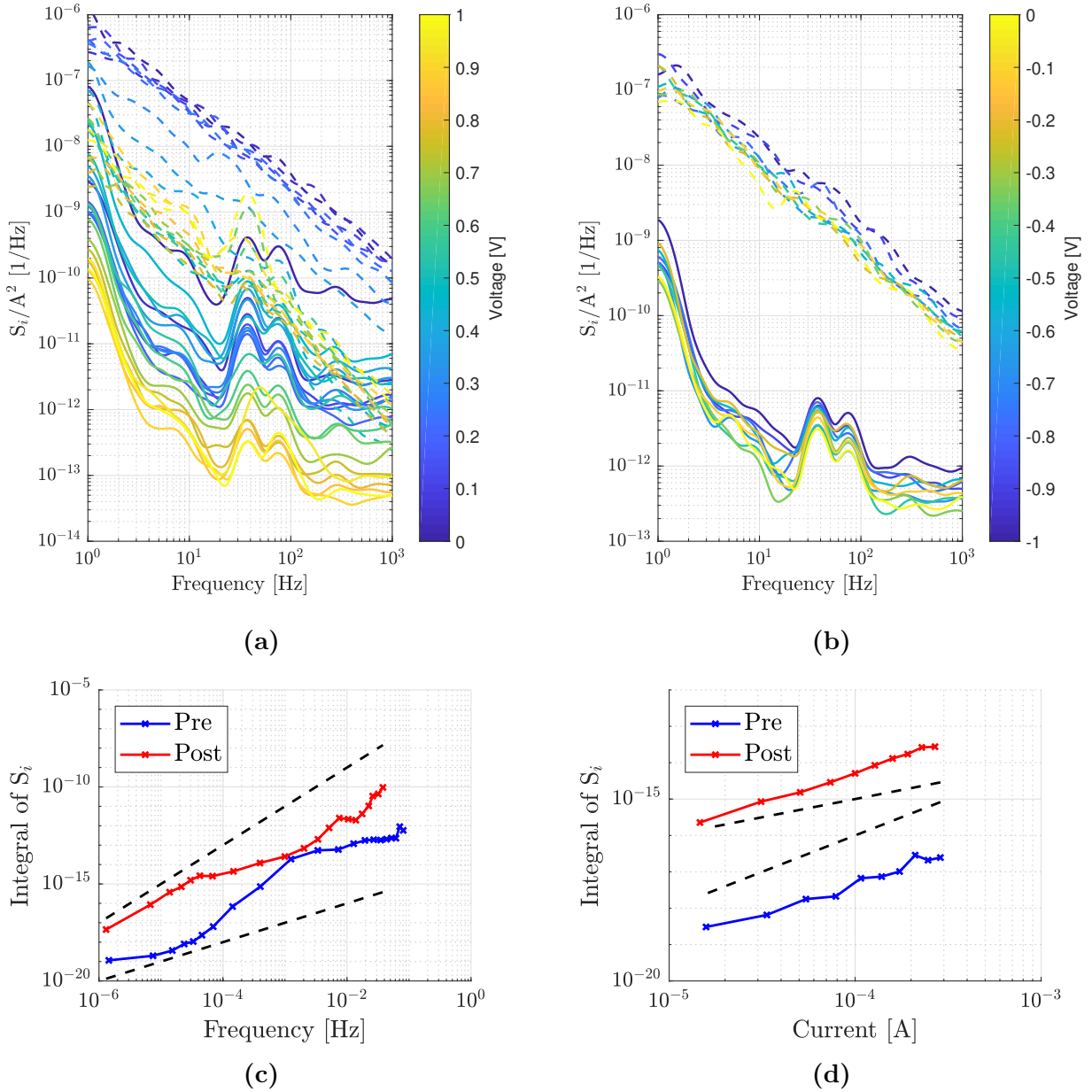
**Figure 4.52:** Apparent doping concentration versus the depth for the silicon solar cell.

#### 4.3.4 Noise

Due to the quantity of information, this section will be divided between the 3 solar cells.

#### CIGS

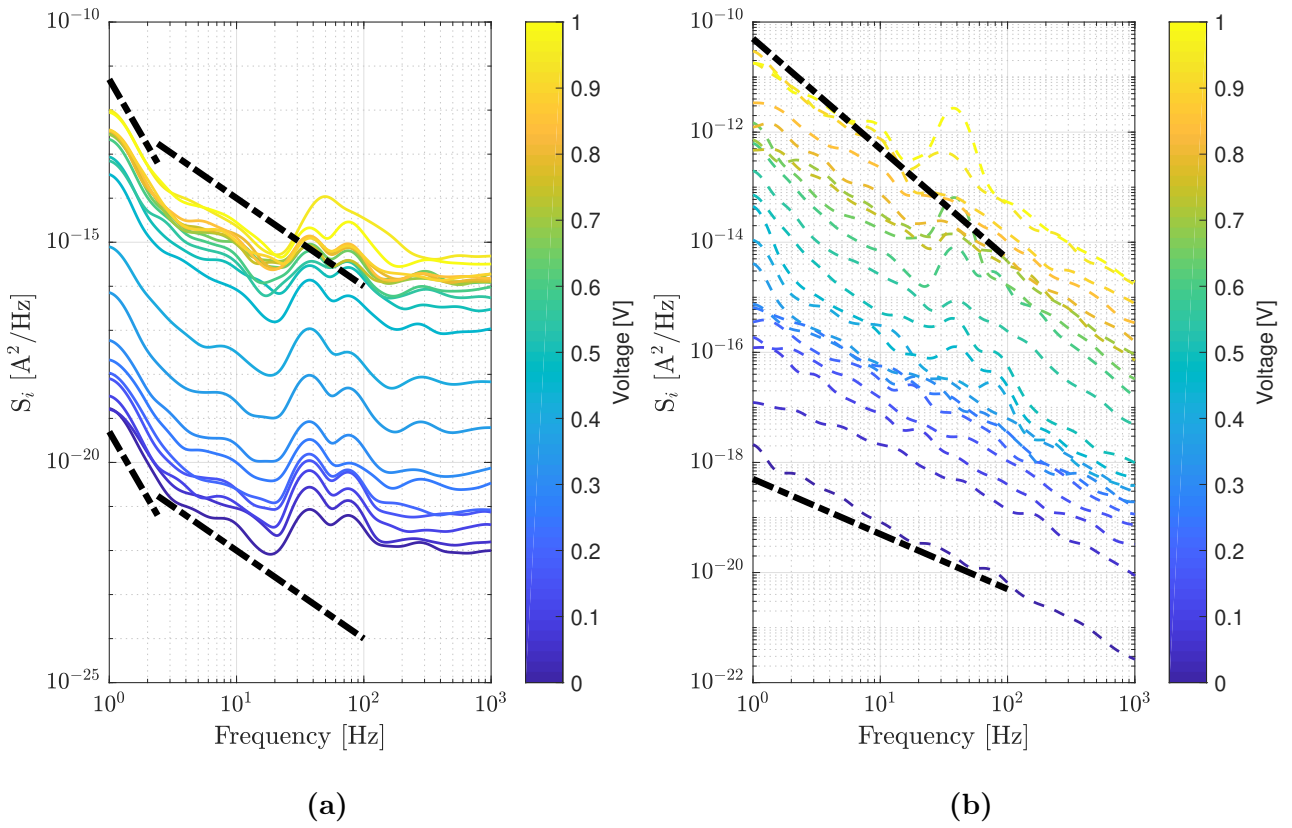
Figure 4.53 a and b presents the spectrum current divided by the current squared. This division is justified by the evolution rather proportional to  $I^2$  than  $I$  of the integral in Figure 4.53 c and d. Concerning the levels of noise, it clearly proves an increase with the radiation which seems more important in the reverse regime.



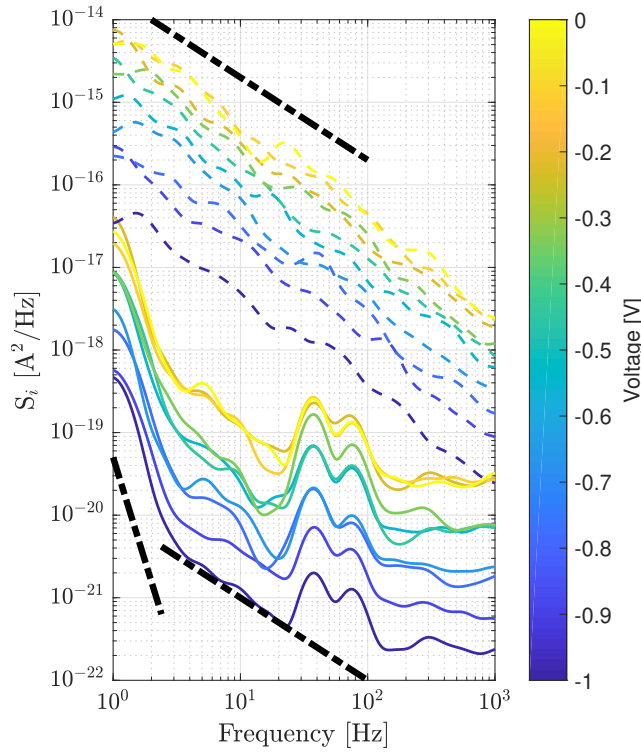
**Figure 4.53:** Current spectrum density divided by the current squared for the CIGS solar cell at different positives (a) and negatives (b) polarisation (in volt) before (full lines) and after (dashed lines) radiation. Figure (c) is the integral of current spectrum versus the current pre and post radiation for the positives voltage while Figure (d) is for the negatives. The first dashed lines for theses two graphs is when  $S_i \propto I$ , the second is when  $S_i \propto I^2$ .

About the different slopes of the spectrums and their evolutions, Figures 4.54 and 4.55 present the current spectrum non-normalised with different proportionalities ( $1/f$ ,  $1/f^2$ , ..) for the positives and negatives polarisations. For the first ones, the pre-radiation follows two different slopes that do not change with the voltage indicating two different mechanisms. The first slope is in  $1/f^5$  until 3-4Hz. Then a more classical  $1/f^2$  slope appears until some contaminations take over. After radiation the behaviour is totally changed. The slope start in  $1/f$  to evolve in  $1/f^2$ . Concerning the mechanism responsible for the  $1/f^5$  slope, it is either destroyed by the radiation or hidden by the newly created defects.

It is the same scenario for the negatives polarisations. The pre-radiations also follows 2 different slopes. The first is in  $1/f^5$  until 3-4Hz and then a  $1/f$  (different from the positives). After the radiation, only the  $1/f$  is still present.



**Figure 4.54:** Figure (a) is the current spectrum density for the CIGS solar cell at different positives polarisation (in volt) pre-radiation. The black bold dashed lines are the different proportionalities: 2 times the  $1/f^2$  and  $1/f^5$ . Figure (b) is the same but after radiation. About the dashed lines, the bottom is for  $1/f$  and the upper for  $1/f^2$ .

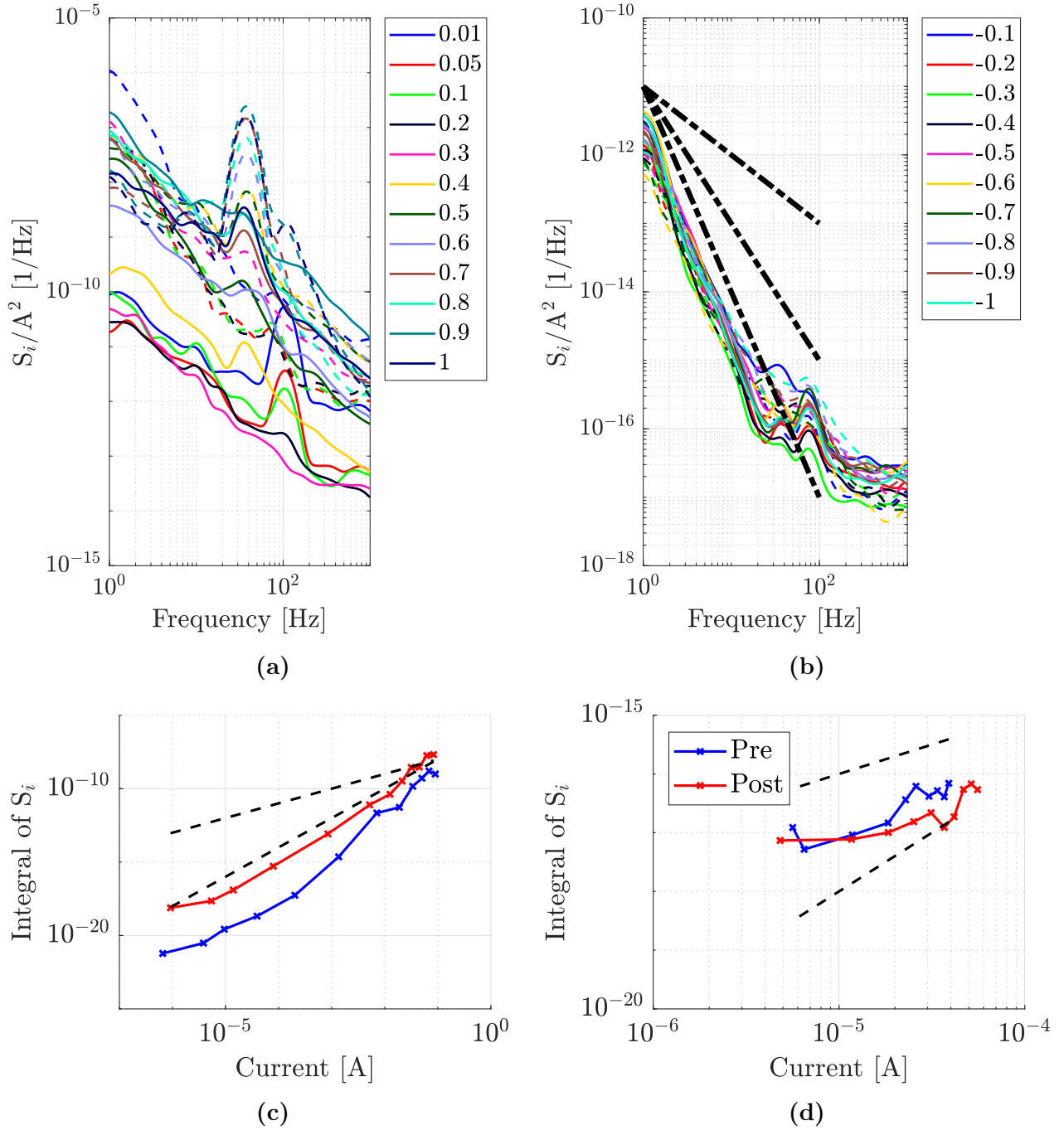


(a)

**Figure 4.55:** Plot of the current spectrum density for the silicon solar cell at different negatives polarisations (in volt) pre and post-radiation. The black bold dashed lines are the different proportionalities:  $1/f$  at the bottom and  $1/f^2$  at the top.

## Silicon

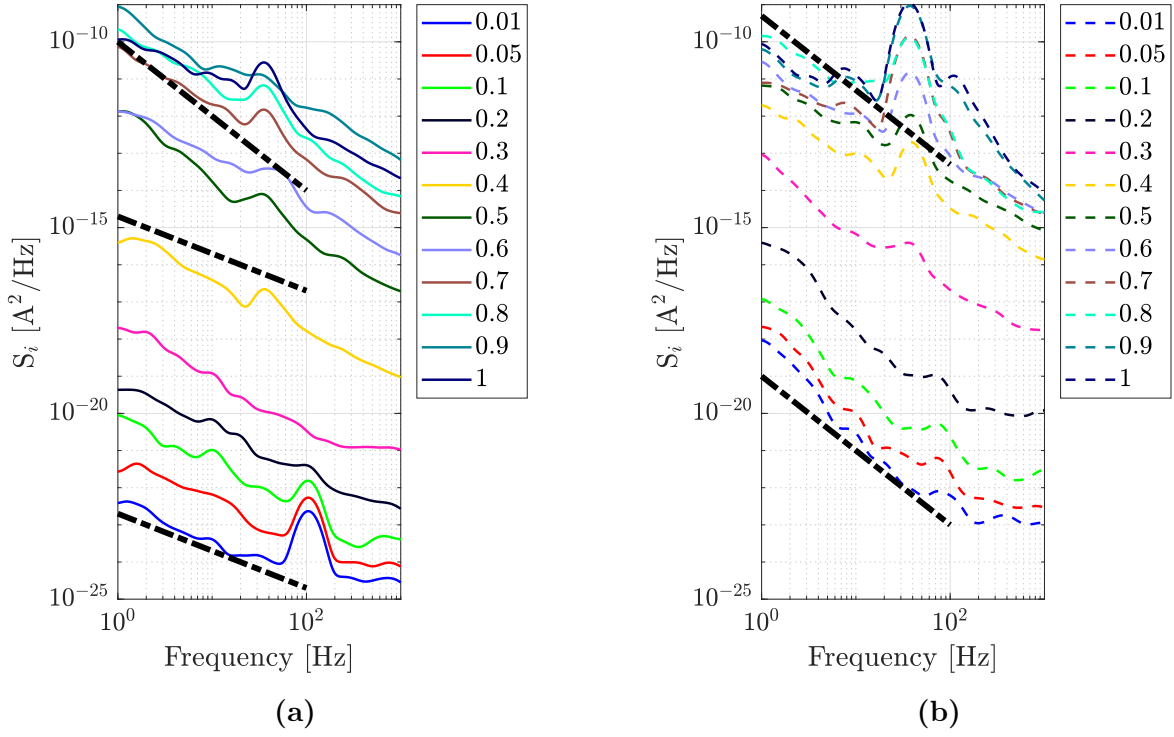
Figure 4.56 presents the normalised current spectrum by the current evolution and the integral of the spectrum versus the current. The latter proves the division by the squared to normalise the spectrum. Both graphs also prove the raising of the noise due to defect created by radiations for the positive voltage only, The noise in the negative voltage does not seems to be impacted by the radiations.



**Figure 4.56:** Current spectrum density divided by the current squared for the silicon solar cell at different positives (a) and negatives (b) polarisations (in volt) before (full lines) and after (dashed lines) radiation. Figure (c) is the integral of current spectrum versus the current pre and post radiation for the positives voltage while Figure (d) is for the negatives. The first dashed lines for theses two graphs is when  $S_i \propto I$ , the second is when  $S_i \propto I^2$ .

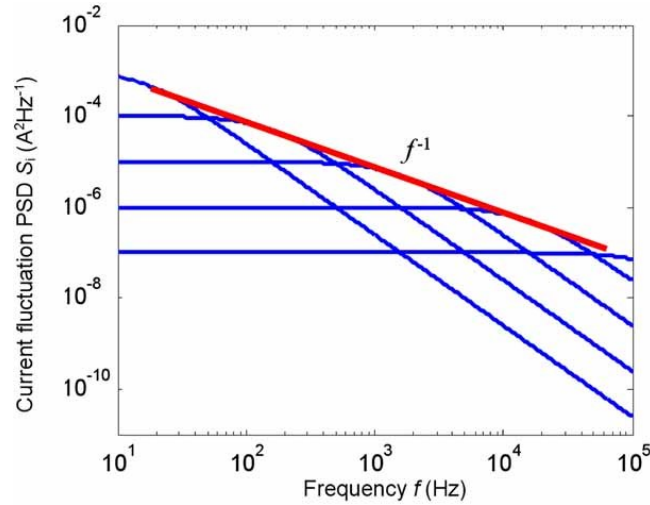
Concerning the mechanisms at play, they stay the same for the negatives polarisation with a slope of  $1/f^3$  (Figure 4.56.b). For the positives ones, presented in Figure 4.57 it is more complex. For the pre-radiation, 2 different mechanisms are at work. The first one as a density decreasing in  $1/f$  until 0.4-0.5V and after the noise is proportional to  $1/f^2$ . While for the post-radiation, it is only proportional to  $1/f^2$ .





**Figure 4.57:** Figure (a) is the current spectrum density for the silicon solar cell at different positives polarisations (in volt) pre-radiation. The black bold dashed lines are the different proportionalities. From the bottom:  $1/f$ ,  $1/f$  and  $1/f^2$ . Figure (b) is the same but after radiation. Both dashed lines are  $1/f^2$ .

Different explanations are possible. One that R. Macku et al. [81] gave is that different sources of noise have a  $1/f^2$  spectrum with different time constant. At low voltage, they interact with each other and the result spectrum is a sum of the different contributions giving a final spectrum of  $1/f$  (see Figure 4.58). Then at higher voltage, a defect becomes majority and the spectrum is in  $1/f^2$ . Thus, after radiation at low voltage, the spectrum is in  $1/f^2$  because the created defects become the majority and there are no more additions.

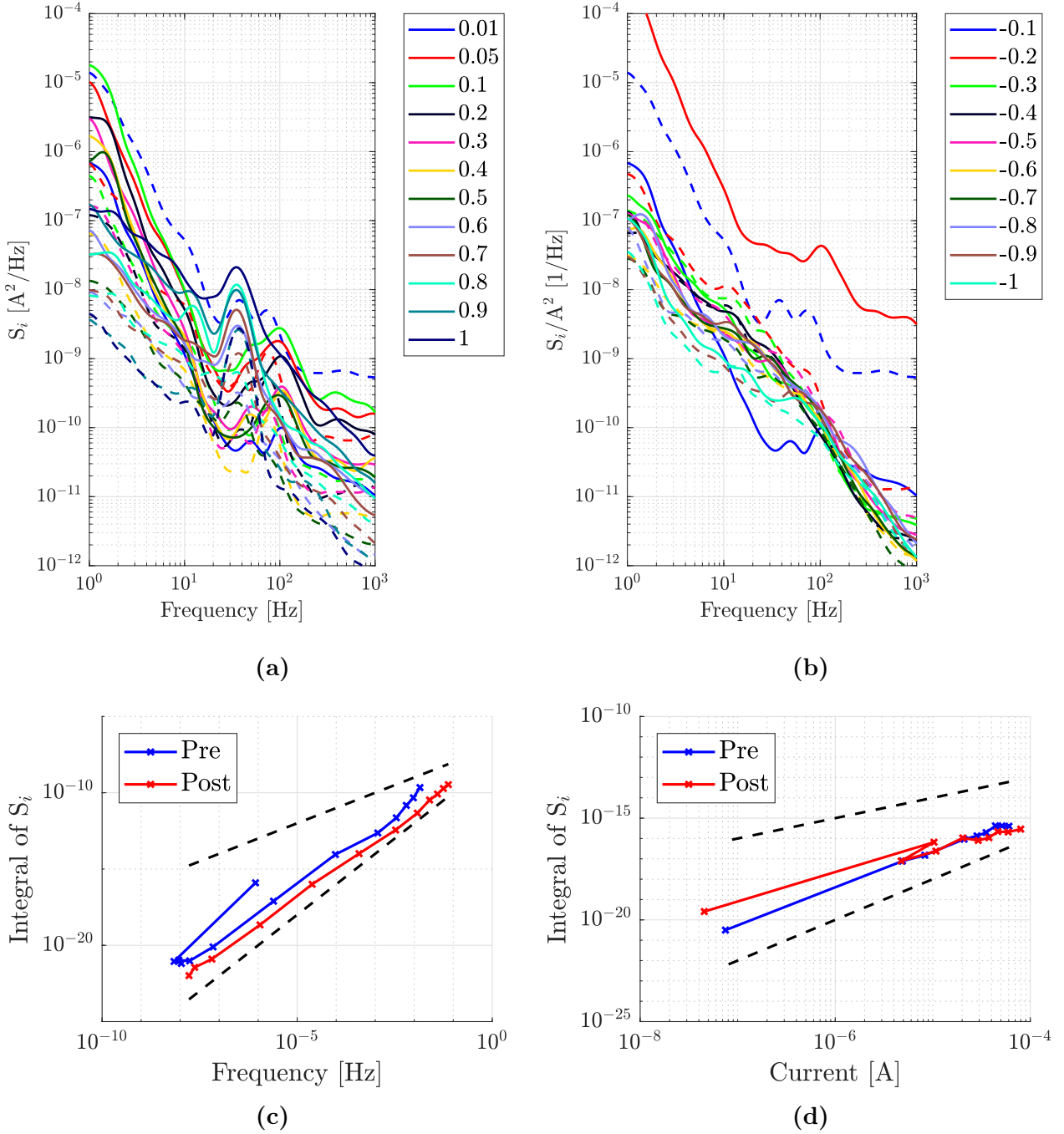


**Figure 4.58:**  $1/f$  noise proposed origin with the addition of multiple  $1/f^2$  noise. From [81].



### Triple-junction

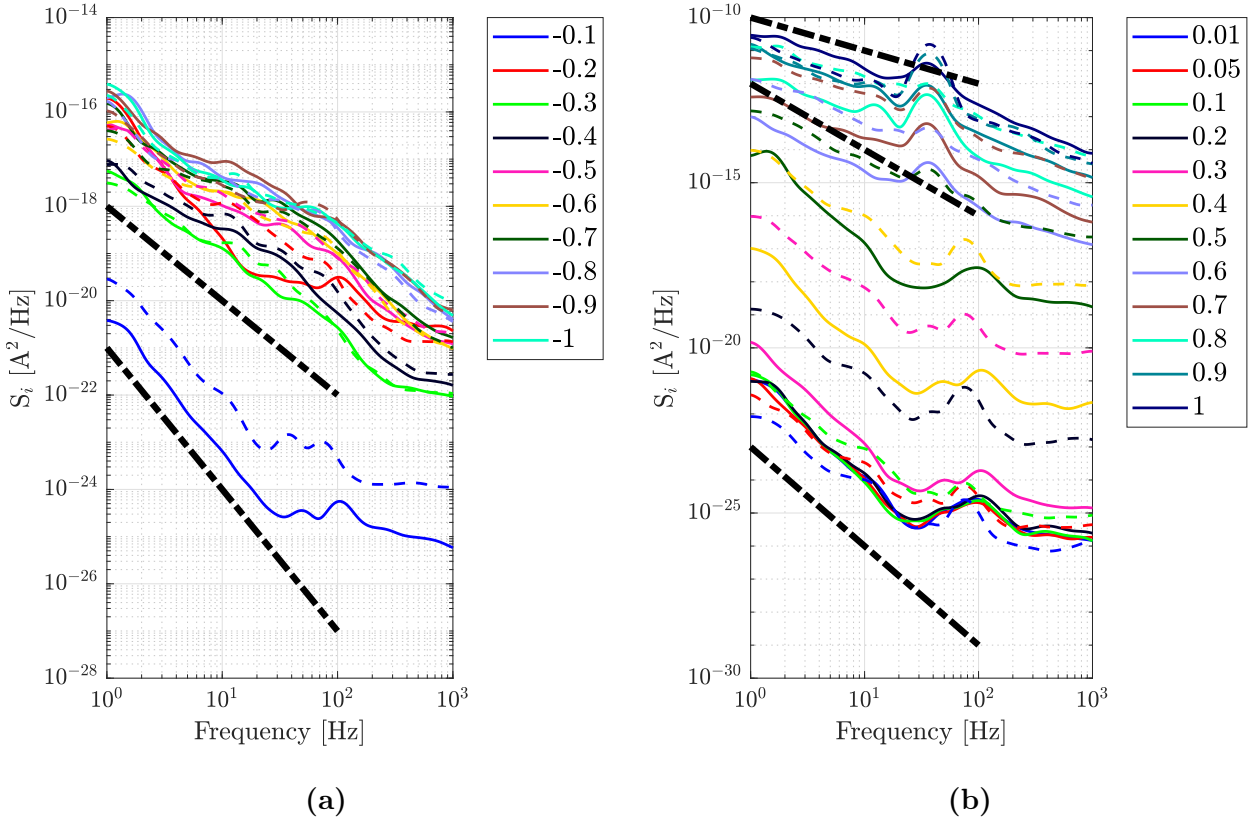
Figure 4.59 presents the different graphs for the triple-junction solar cell. Both spectrum are normalised by the current squared in view of their integral's evolution. It also shows that the noise does not seems to be affected by the radiations, neither in positive nor negatives voltages.



**Figure 4.59:** Current spectrum density divided by the current squared for the triple-junction solar cell at different positives (a) and negatives (b) polarisations (in volt) before (full lines) and after (dashed lines) radiation. Figure (c) is the integral of current spectrum versus the current pre and post radiation for the positives voltage while Figure (d) is for the negatives.

The first dashed lines for these two graphs is when  $S_i \propto I$ , the second is when  $S_i \propto I^2$ .

Concerning the evolution of the slope with the voltage, it is more complicated than the two others cells. It seems that the slopes is related to the bias. For the negative (see Figure 4.60), the lowest spectrum values have a slopes of  $1/f^3$  and after  $10^{-18}$  A<sup>2</sup>/Hz, the slope is  $1/f^2$  for the rest of the curves. It is the same principle for the positives ones. It start with a slope of  $1/f^3$ , arriving near  $10^{13}$ , then, there is a transition to  $1/f^2$  to finish with a  $1/f$  around  $10^{-10}$  A<sup>2</sup>/Hz.



**Figure 4.60:** Figure (a) is the current spectrum density for the silicon solar cell at different negatives polarisations (in volt) pre and post-radiation. The black bold dashed lines are the different proportionality. From the bottom:  $1/f^3$  and  $1/f^2$ . Figure (b) is positives voltages with the dashed lines being  $1/f^3$ ,  $1/f^2$  and  $1/f$  (from the bottom).

#### 4.3.5 Summary

In summary, three different solar cells (CIGS, Silicon and triple-junction) were irradiated by protons at 10MeV. Then, they were analysed using light IV, dark IV, dark CV and noise.

Concerning the light IV, only the silicon and triple-junction were measured. Indeed, the setup was not equipped to measure correctly small solar cells, like the CIGS. An other problem for the triple junction was that this cell is calibrated to work in space (spectrum AM0) while the device measures with a spectrum AM1.5. This gave the sudden drop at low voltage since there are 1 or 2 subcells that produce current. As for the irradiation, both cells were impacted. The silicon was the most degraded with an efficiency drop of 6.5% while the other was reduced by 5.1%. Since the filling factor (FF) was not too impacted for both cells, their shunt and series resistance should not be too impacted.

For the dark IV, the two diodes model was fitted on the IV curves pre and post-radiation of the silicon and CIGS solar cell. For the triple-junction, the simpler 1-diode model was applied. The

CIGS results showed that only the series resistance were impacted during radiation due to the cell thickness. Indeed, since it is a thin solar cell, the protons went through with most of the damage done at the back contact. Regarding the silicon solar cell,  $J_1$  was deteriorated while  $n_1$  was improved. It points to defects created in the base region of the cell [74]. Furthermore, for the triple-junction,  $J_1$  was also degraded. However, this time, it was due to the model. In reality, the threshold voltage was reduced. Indeed, the tunnelling between the subcells was easier due to defects created in the bandgap: the charge carrier went through a defect state before decaying to the other band on the other side of the junction.

Regarding the CV measurements, only pre-radiation for the silicon and pre and post-radiation for the CIGS PV cell gave interpretable measures. For the CIGS, measures showed that the CV was slightly changed by radiation. For the extraction of the apparent doping ( $N_{cv}$ ), pre and post-radiation results followed the same trend until 400nm. After,  $N_{cv}$  post-radiation increased, and it could indicate where defects were created. Concerning the silicon, the measure at 100kHz followed a different trend, even after being corrected. Coupling this with the Nyquist plot that showed the imaginary part seems equal to the real part for the 100kHz curve, it may indicate that the quasi-static condition was overreached. If this is the case, the lifetime in the solar cell is between 1.6 and 16 $\mu$ s. Then, the apparent doping was extracted and it was in the values reported for a silicon solar cell.

Finally, for the noise measurement, only a qualitative analyse was made. First, the different current spectrum density had been divided either by the current or the current squared. The choice was made by looking at the integral of the spectrum versus the current. Then, the spectrum was divided by how the integral varies with the current ( $I$  or  $I^2$ ). It was done to compare the level of noise before and after radiation. The results showed an increase of noise for the CIGS (at positives and negatives polarisations) and the silicon solar cell (only for the positives polarisations). Regarding the triple-junction, the noise was not increased. Lastly, the evolution of the current spectrum density slope was investigated and nearly all were impacted by the radiation, showing a change in the different mechanisms at play.

# Chapter 5

## Conclusion

### 5.1 Summary

In conclusion this work analysed two subjects linked to the solar cell. The first covered the study of passivation and carrier selective layer to increase its efficiency. The second one developed the study of 3 different solar cells (triple-junction gallium based, silicon and CIGS) after irradiation. To do so, this thesis is divided into five chapters, finishing with the conclusion.

The first and second chapters lay the context and introduce the different theoretical concepts encountered. First, it explained the interest of increasing the efficiency of solar cells due to global warming. Indeed, the climate report from IPCC is clear and without appeal, the climate is warming up and human emission are the causes. It urgently needs to decrease with the help of different low-carbon technologies like the solar cell. For this subject, a lot of research is conducted to decrease the extrinsic losses, either optical or electric. For the latter, the interface represents the next challenge. Because of the change in symmetries or the deposition process, there is a considerable amount of defects in this zone. These imperfections are the place of energy losses due to the recombination of holes and electrons by the Shockley-Read-Hall mechanism. Three techniques may be used to mitigate their effect: field-effect passivation, passivation layer, and carrier selective layer. Only the last two were studied in this work. For the passivation layer, it consists of a deposited layer that will link to the dangling bonds. For a silicon wafer, an equivalent is to grow a thermal  $\text{SiO}_2$  and annealing with hydrogen. The two atoms will link to the unlinked silicon atoms. The second experimented technique was the carrier selective contact. The deposited layer will "repulse" the electrons of the hole contact due to band alignment or band bending. The material used for hole selective is generally a metal oxide with a high work function. The ones used in this work were nickel and tungsten oxide. Chapter 2 also gave a proposal for a mathematical definition of selectivity, which could not be measured in this work.

These chapters also explain the role of solar cells in space, the influence and sources of the radiation to which they are subject. It appears that the degradation mechanism due to this environment is the atomic displacements: the radiation transfers its energy to the atom that can move from its position, creating a defect, leading to efficiency losses. Then, the different artificial radiation sources to simulate a stay of 15 years in space were discussed. The proton irradiation was chosen for its ability to do atomic displacement. Finally, the time and energy of radiation was calculated using the displacement damage equivalent fluence method. However, since it gives a radiation time of over 30 hours, it was decided to only irradiate the three solar cells for 1 hour at 10 MeV.

The third chapter starts with describing the different processes, like the  $\text{SiO}_2$  growth or the oxide deposition, done to build the stacks used to study the two metal oxides. There were 3 stacks, one for the electrical measurement with aluminium back contact, one symmetrical for the lifetime and one with a thicker oxide to analyse its intrinsic characteristics. It was followed

by the presentation of the three cells and their structure. Then, it concludes with a description of the different measures and equipment used in this work. Some of them were used to assess and compare the results with the literature. In comparison, others were done to characterise the samples and extract their intrinsic properties.

Finally, chapter four is divided into 3 sections: characterisations, performance and PV cell under radiations. The first section shows the different measurements to characterise or confirm what had been deposited in Winfab. It starts with the measures done with the XPS. It allowed to confirm the thickness of the SiO<sub>2</sub> deposited (2.9nm), the good quality of the NiO deposited and the problem with the metal layer oxidation (MLO) recipe. This recipe decoupled the deposition and oxidation and was developed due to defects created during the deposition process. The XPS highlighted that the 3nm of nickel deposited was not fully oxidised. Then, the XRD was used to check the crystallinity of the metal oxide before and after the annealing. The major find is that the silicon and the tungsten oxide interface may have mixed to form either tungsten silicide or SiO<sub>2</sub>. It is possible that it only does this to this type of stack since the WO<sub>3</sub> is in direct contact with the silicone, while the others have a 3nm layer of SiO<sub>2</sub> between the two materials. It is followed by the measure of the bandgap by the tauc method. Both oxides have an opposite trend, the NiO decreased with the annealing while the WO<sub>3</sub> increased. The values found for this one were superior to what was typically found in the literature. The stress inside the material due to the deposition may explain it, but more measurements are required to confirm it. Lastly, the mobility of each metal oxide was found between -0.3 and 0.3 cm<sup>2</sup>/V.s. It could not go lower in precision because of the two techniques used. For one, the mobilities were below its detection limit. And for the second, there was a problem with the wafer resistivity, which prevented performing the measure.

The second section is about the performance, through lifetime, CV and IV measurements, of the two metal oxides and the silicon oxide as a passivation and hole selective layer. The first analysed metric was the minority carrier lifetime. It was established that the reactive sputtering completely ruined it because it decreased from 234 $\mu$ s (SRV: 77cm/s) to 4 $\mu$ s (5100 cm/s) for the NiO and 2 $\mu$ s (9700 cm/s) for the WO<sub>3</sub>. This massive reduction after the deposition pointed to the apparition of defects during it. The cause was the oxygen ionised by the plasma that hit the wafer. That was the reason why the MLO recipe done without plasma was developed. The plasma can also explain the lifetime difference between the NiO and WO<sub>3</sub> as it was set at higher power (100W) than the NiO (50W). Then, the second metric was obtained using CV measurements. The various curves were analysed after pointing out where the dispersion was greater than 0.5% and corrected using the 6-element model. All of them were subjected to a flatband shift caused by the increase of majority carrier in the oxide. Afterwards, the density of trap ( $D_{it}$ ) was reviewed. Before the oxide deposition, the SiO<sub>2</sub> had a density of 1.2E12 cm<sup>-2</sup>eV<sup>-1</sup> which was slightly higher than the literature (1-10E11 cm<sup>-2</sup>eV<sup>-1</sup>) and kept the value high for the rest. The thickness of NiO seemed to reduce the density for an unknown reason, while the annealing of WO<sub>3</sub> clearly reduced it to the point to go lower than the start. It proved that annealing neutralized the defects. The last measures done with the CV was to assess the mobile charge with a hysteresis. It was only done on WO<sub>3</sub> and it clearly showed that the charges came from the SiO<sub>2</sub> oxide, which were reduced by the annealing. The measure was done at 1kHz and 10kHz and exhibited a sign change between the two. It was thus supposed that fewer defects near the interface are probed at 10kHz, indicating a change of mechanism (a charge injection either from the Si/SiO<sub>2</sub> or the gate/WO<sub>3</sub> interface) between the two frequencies. Lastly, the conduction mechanisms were analysed with IV measurements. Multiple were proposed, like the variable-range-hopping or the Poole-Frenkel, that dominated at a different voltage. Additional measurements with temperature variations are needed to discriminate all of the

proposed mechanisms.

As for the third section, it presents the results of the three solar cells (CIGS, silicon and triple junction) that were irradiated by protons at 10MeV for 60 minutes. The first measure done was light IV and only the silicon and triple junction were measured. They presented different tendencies before radiation since the equipment has not the right spectrum to activate the three-junction of the triple-junction solar cell. Consecutively, only 1 or 2 had produced some current which explained a sudden drop in the result. Concerning the radiation, both were impacted but harder for the silicon, with a drop in the efficiency of 6.5% and 5.1% for the triple. The dark IV measures gave interesting results in function of the structure of the cell. Indeed, the two-diode model was applied and the degradation of parameters was different for each cell. Only the series resistance was impacted for the CIGS due to the high energy the proton had which went through the whole cell, damaging the back contacts. For the silicon cell, the current density of the first diode representing the diffusion was deteriorated while the ideality factor was improved. These pointed to defects created in the base region of the solar cell. As for the triple junction, the threshold voltage was reduced because the tunnelling was easier between the cells due to defects created in the bandgap of the material that separates them. Afterwards, CV measurements were done. All the cells were measured, but the silicon post-radiation were too damaged and the triple-junction too complicated to analyse. After removing the influence of the series resistance, the apparent doping ( $N_{cv}$ ) versus the depth was extracted to analyse where the radiation had created the defects. The values post radiation found for the CIGS showed an increase of  $N_{cv}$ , the defects, at the end of the cell, explaining why the series resistance was impacted. As for the silicon, the measure at 100kHz did not respect the quasi-static condition, giving an estimation of the carrier lifetime in the cell. For  $N_{cv}$ , the values correspond to what is found in the literature. Finally, the last measure done on the solar cells were noise measurements. The analysis was more qualitative than quantitative. The proportionality of the current spectrum versus the current was found via its integral (either linear or squared). It is then divided by it to reveal if the radiation had increased the noise or not. It only increased for CIGS (positive and negative polarisation) and the silicon (only positives). Lastly, the change of current spectrum slope was investigated and nearly all were impacted, proving a change of the dominant noise mechanism.

## 5.2 Further researches

It remains a lot of unanswered questions concerning the tungsten and nickel oxide as hole selective layer. First, the definition of selectivity in the theoretical background section which can provide a more robust plan to compare the metal oxide. Regarding the comparison, this thesis could not compare the two oxides with the different measures due to defects created during the deposition. Thus, other techniques can be tried like RF sputtering and thermal evaporation to minimise the creation of defects during it. The metal layer oxidation technique can be another candidate if the recipe is improved to oxidise the whole layer. Thirdly, more measurements are required (with temperature variation) to identify the different mechanisms of tunnelling present for NiO and redo the one on  $WO_3$  in order to confirm the asymmetrical IV trend of the nickel oxide. Lastly, simulations are needed to fully understand the diverse impacts of different parameters like doping or thickness for this subject.

As for the solar cell, the noise measurement can be refined to understand the mechanism before and after radiation. The impact of fluence can be studied as well. Additional research can be led with the decrease of the radiation time and more specially with the increase since the initial calculation planned an irradiation time 30 times longer, to study the evolution of the efficiency.

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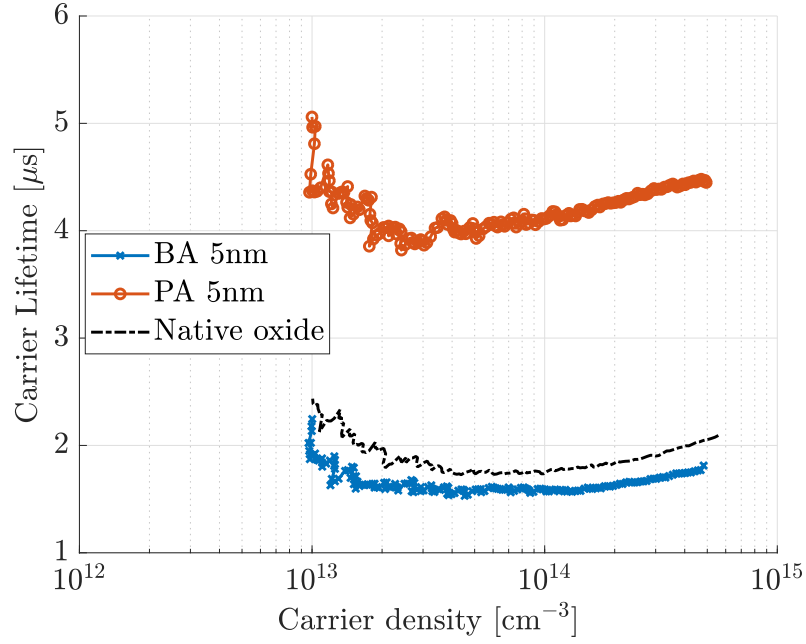
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# A Additional data - Mobility

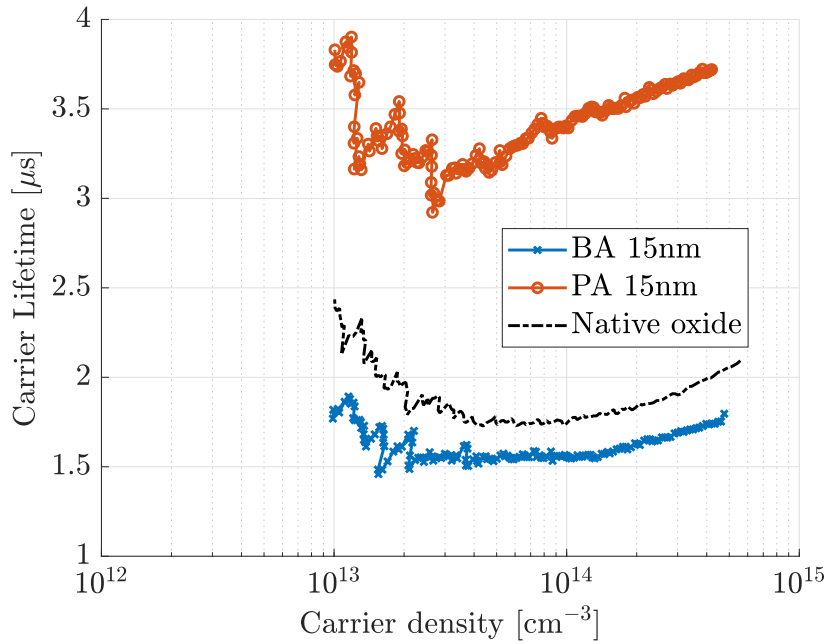
| Process: Four Probes<br>Resistivity Measurement |               |              |             |              |
|-------------------------------------------------|---------------|--------------|-------------|--------------|
| Probes Source Meter                             | 12 43         | 23 14        | 34 21       | 41 32        |
| Current 1 (A)                                   | 9.9838E-09    | 9.9861E-09   | 9.9861E-09  | 9.9853E-09   |
| Voltage 1 (V)                                   | .30265        | .21178       | .3057       | .21763       |
| Current 2 (A)                                   | -9.9937E-09   | -9.9933E-09  | -9.9933E-09 | -9.9933E-09  |
| Voltage 2 (V)                                   | -.30715       | -.21255      | -.30345     | -.20672      |
| Resistance (Ohm)                                | 3.052434E+07  | 2.123838E+07 | 3.04889E+07 | 2.124023E+07 |
| Ratio                                           | .6957849      | .6965936     | .6966543    | .6958455     |
| Form Factor                                     | .991033       | .991105      | .9911103    | .9910383     |
| Resistivity (Ohm*cm)                            | 581.2589      | 580.9031     | 580.9271    | 581.2828     |
| Process: Four Probes<br>Hall Measurement        |               |              |             |              |
| Probes Source Meter                             | 13 24         | 24 31        | 13 24       | 24 31        |
| Current 1 (A)                                   | 9.9868E-09    | 9.9861E-09   | 9.9861E-09  | 9.9868E-09   |
| Voltage 1 (V)                                   | -.093151      | .098438      | -.093334    | .098598      |
| Current 2 (A)                                   | -9.9937E-09   | -9.9933E-09  | -9.9925E-09 | -9.9941E-09  |
| Voltage 2 (V)                                   | .093322       | -.086894     | .093444     | -.087093     |
| Resistance (Ohm)                                | -9332750      | 9276155      | -9348903    | 9293426      |
| Field (G)                                       | 8008.6        |              | -7850.4     |              |
| Temperature (K)                                 | 310           |              |             |              |
| Resistivity (Ohm*cm)                            | 581.093       |              |             |              |
| Mobility (cm <sup>2</sup> /Vs)                  | -3.032916E-02 |              |             |              |
| Density (cm <sup>-3</sup> )                     | -3.541861E+17 |              |             |              |
| Hall Coeff. (cm <sup>3</sup> /Coul)             | -17.62406     |              |             |              |
| Sheet Number (cm <sup>-2</sup> )                | -1.77093E+12  |              |             |              |
| Sheet Res. (Ohm/cm <sup>2</sup> )               | 1.162186E+08  |              |             |              |
| Type of Carriers                                | electrons     |              |             |              |

**Table 20:** Example of mobility measurement for NiO. The measure is below its detection limit thus the measure is wrong and the type of carriers is noted electrons instead of holes.

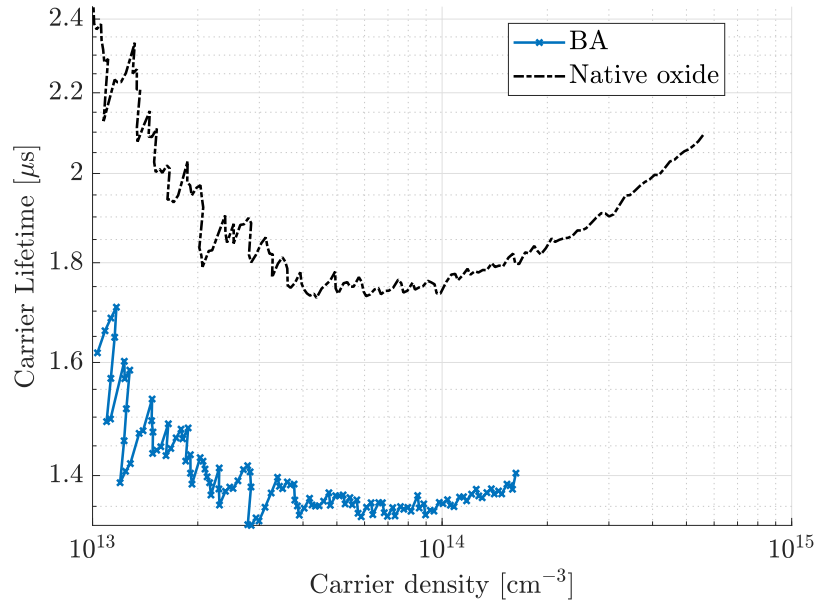
## B Additional data - Lifetime



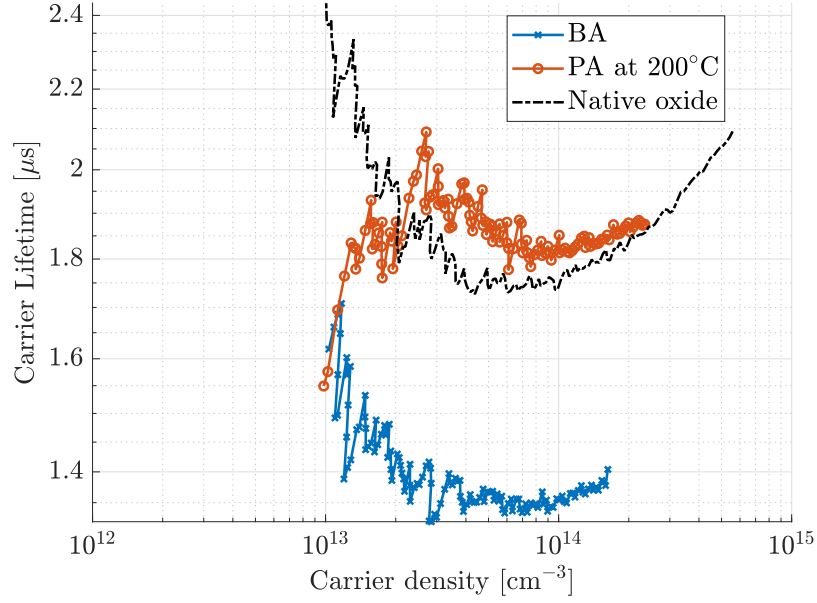
**Figure B.1:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the NiO 5nm before/post annealing (BA and PA).



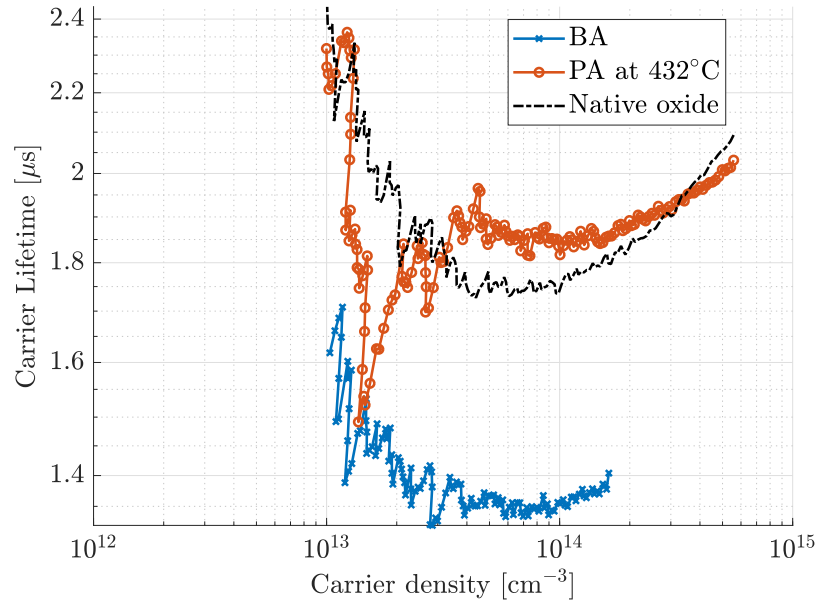
**Figure B.2:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the NiO 15nm before/post annealing (BA and PA).



**Figure B.3:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the  $\text{WO}_3$  with no annealing.



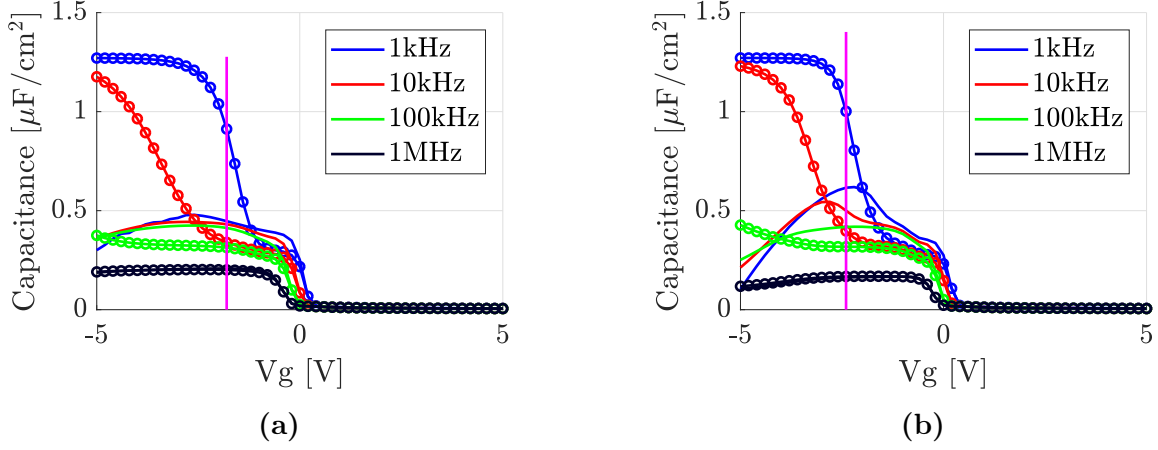
**Figure B.4:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the  $\text{WO}_3$  before/post-annealing (BA and PA) at  $200^\circ\text{C}$ .



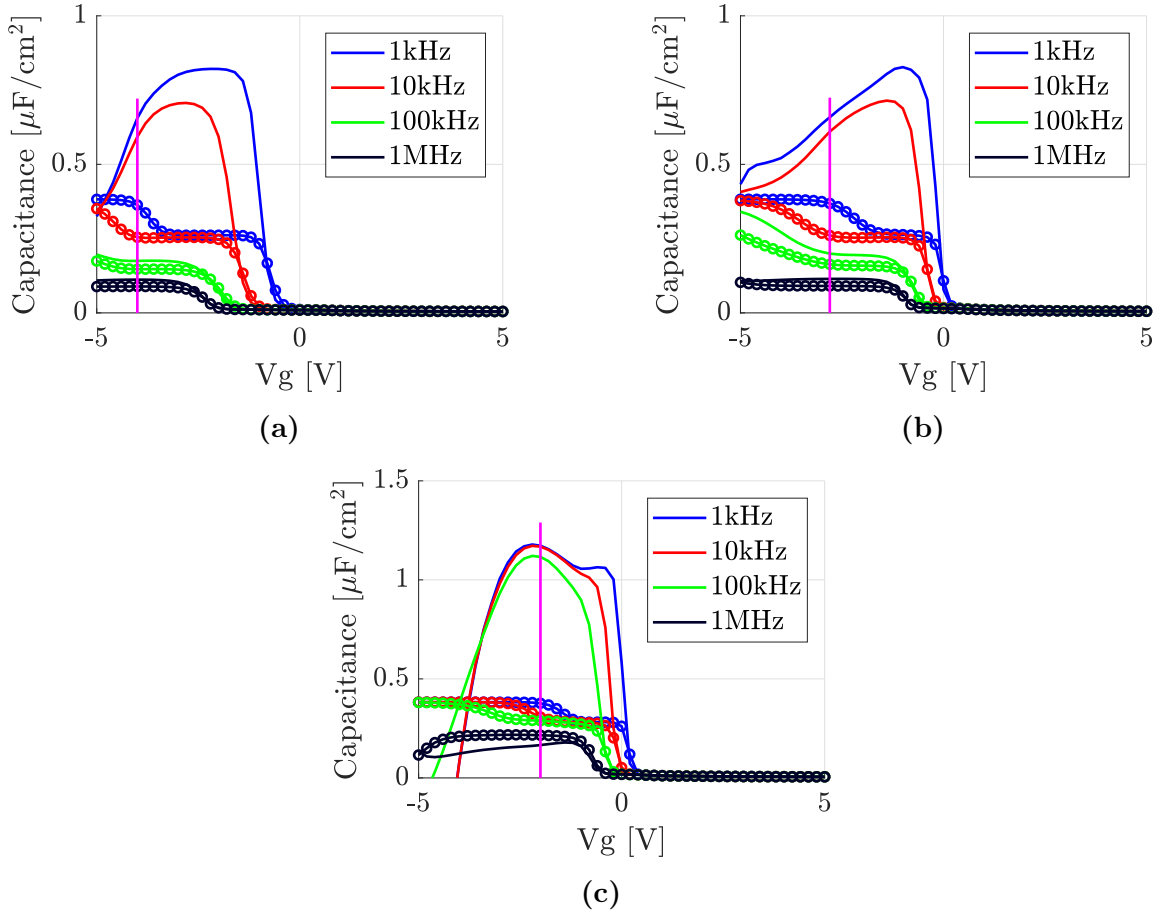
**Figure B.5:** Injection-dependent effective minority carrier lifetime measurements for the native oxide and the  $\text{WO}_3$  before/post-annealing (BA and PA) at 432°C.

# C Additional data - CV

## C.1 Capacitance correction



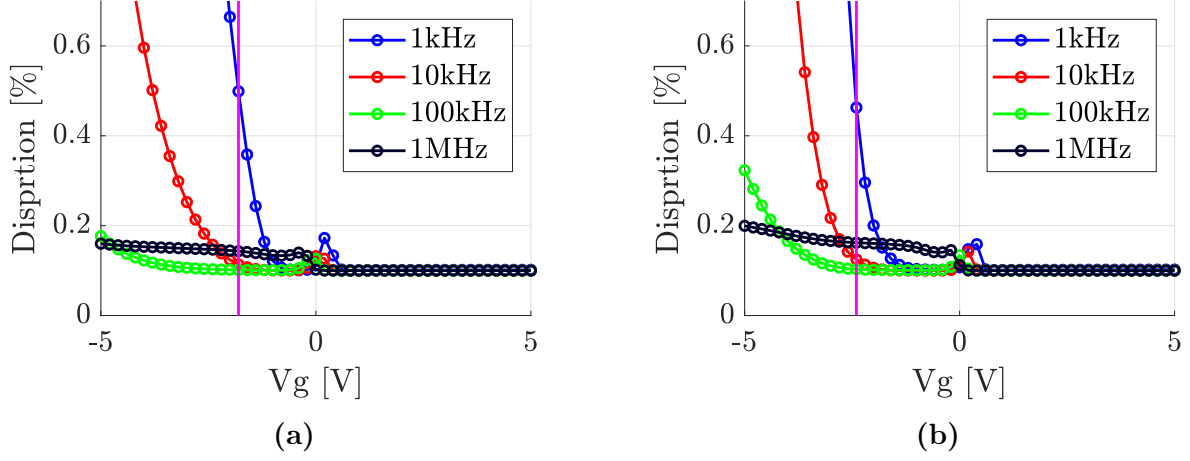
**Figure C.1:** CV measurements with their respective correction for NiO 10nm (a) and 15nm (b). The marked lines are the corrections while the other are the actual measurements. The right of purple line indicates a dispersion below 0.5%.



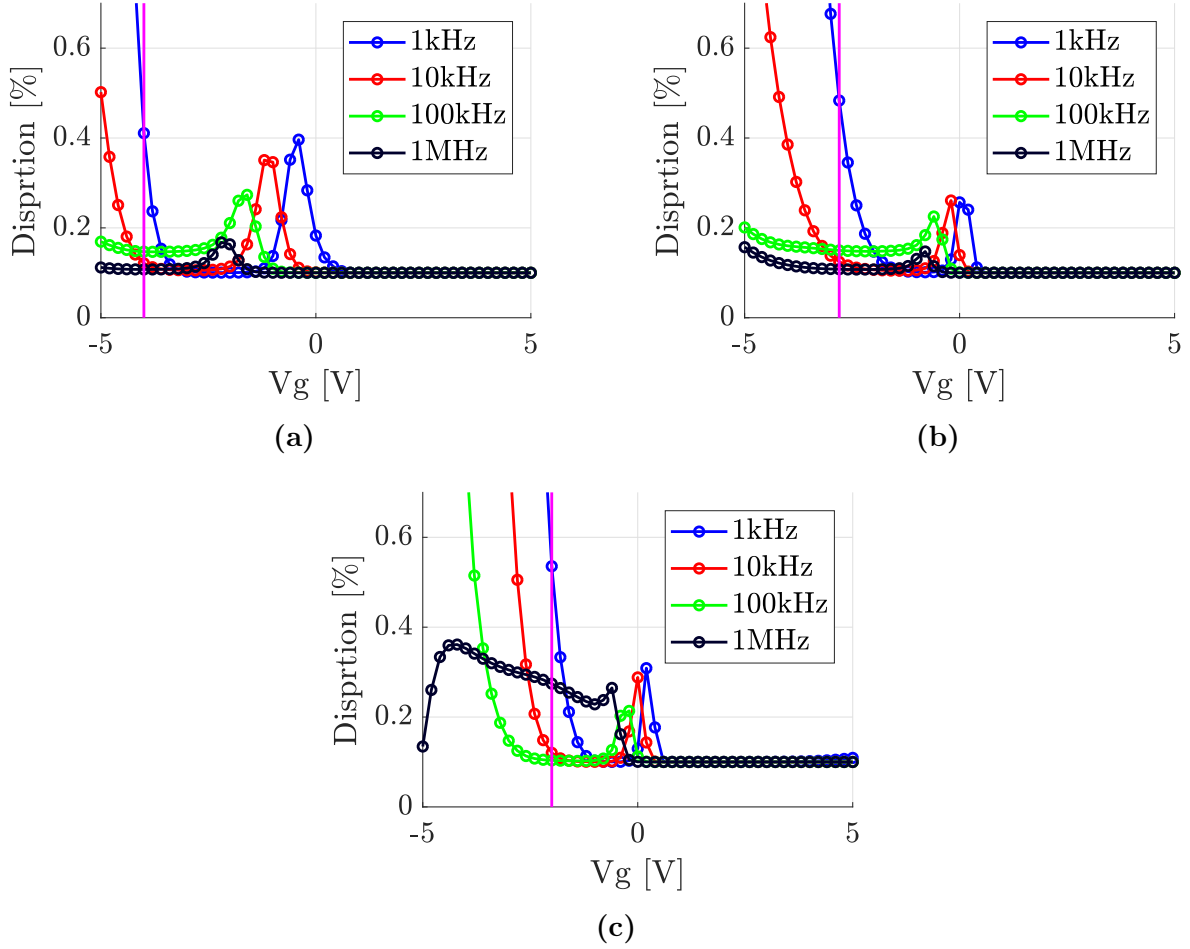
**Figure C.2:** CV measurements with their respective correction for  $\text{WO}_3$  not annealed (a), annealed at 200°C (b) and 432°C (c). The marked lines are the corrections while the other are the actual measurements. The right of purple line indicates a dispersion below 0.5%.



## C.2 Dispersion

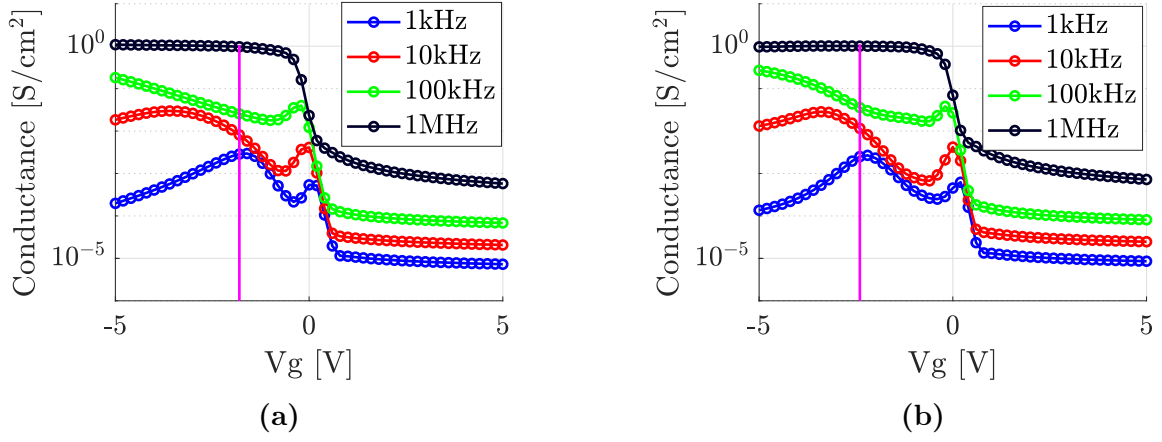


**Figure C.3:** Dispersion for NiO 10nm (a) and 15nm (b). The right of purple line indicates a dispersion below 0.5%.

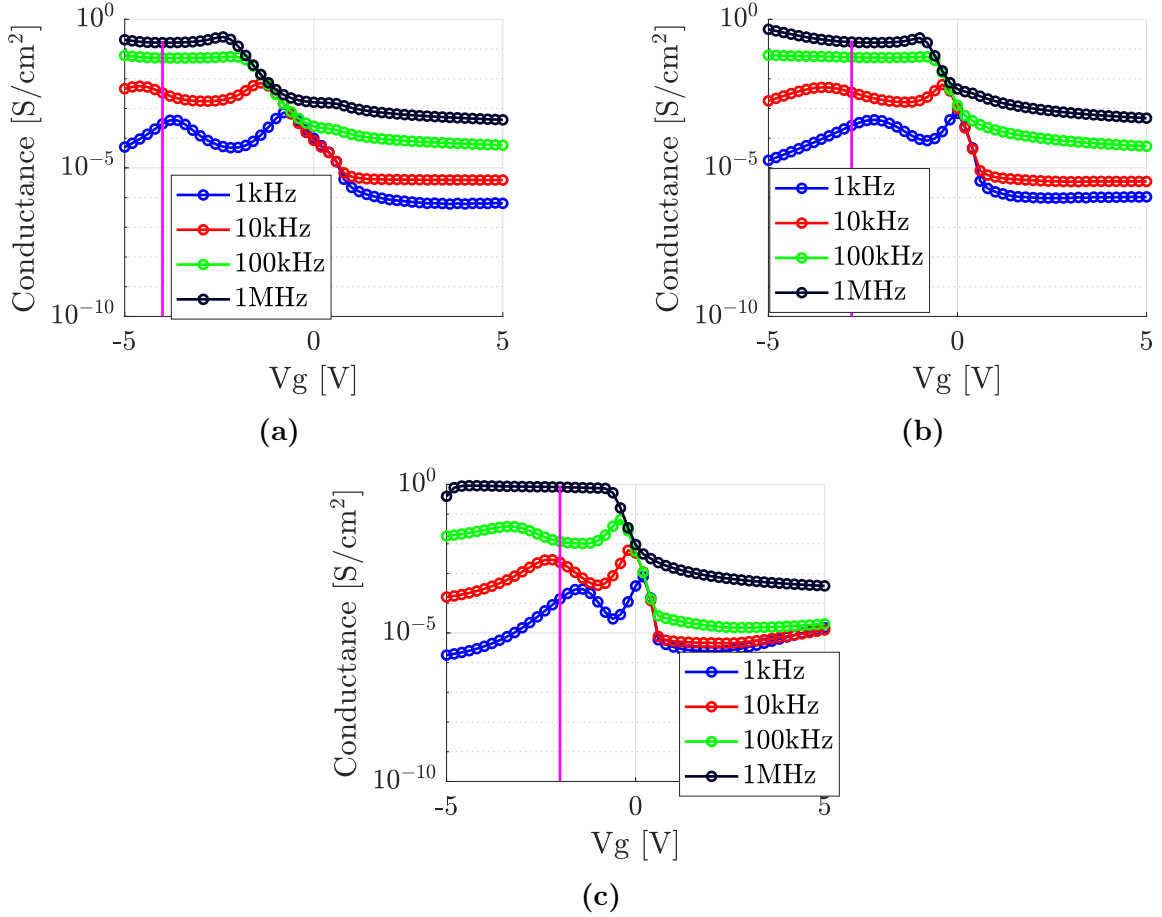


**Figure C.4:** Dispersion for WO<sub>3</sub> not annealed (a), annealed at 200°C (b) and 432°C (c). The right of purple line indicates a dispersion below 0.5%.

### C.3 Conductance

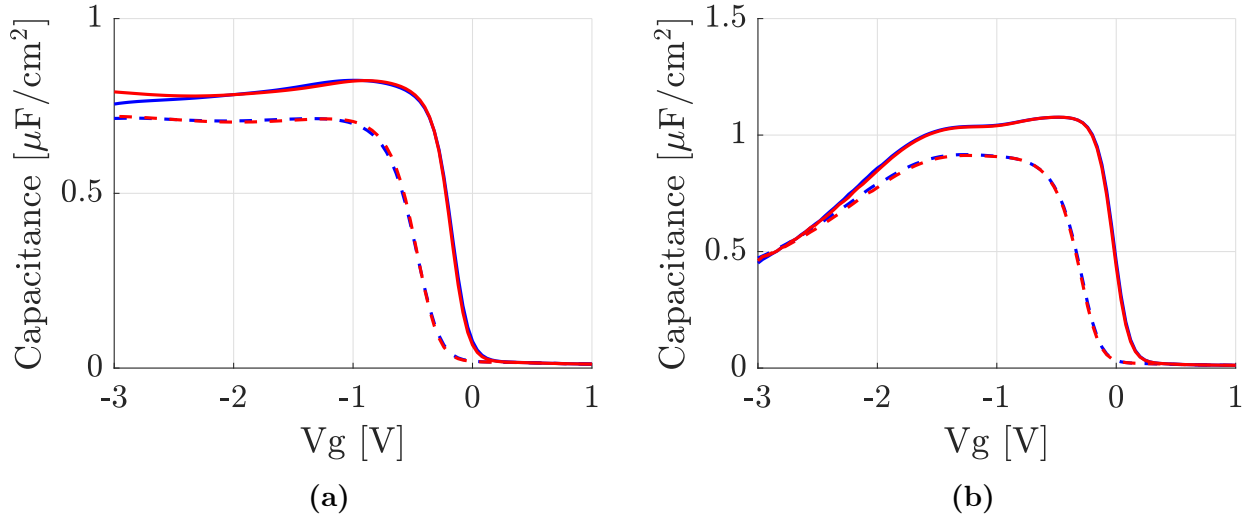


**Figure C.5:** Conductance-voltage measurements with their respective correction for NiO 10nm (a) and 15nm (b). The marked lines are the corrections while the other are the actual measurements. The right of purple line indicates a dispersion below 0.5%.



**Figure C.6:** Conductance-voltage measurements with their respective correction for WO<sub>3</sub> not annealed (a), annealed at 200°C (b) and 432°C (c). The marked lines are the corrections while the other are the actual measurements. The right of purple line indicates a dispersion below 0.5%.

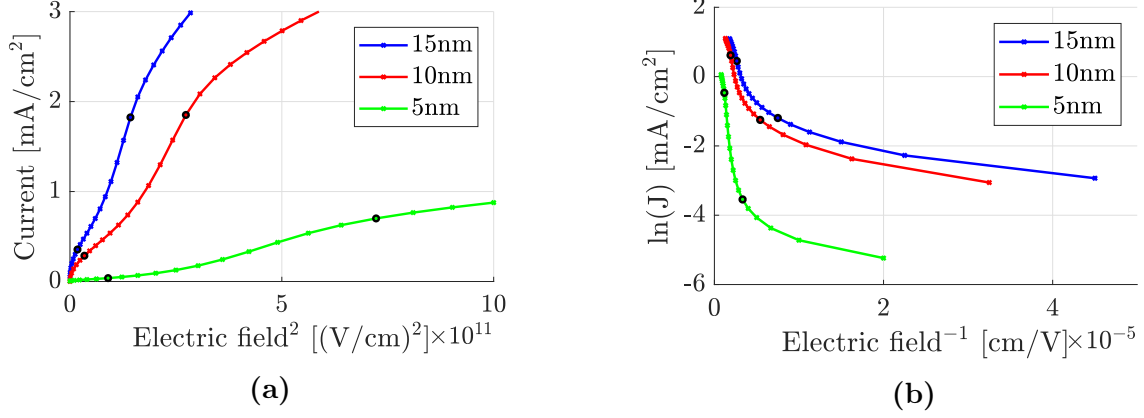
## C.4 Hysteresis



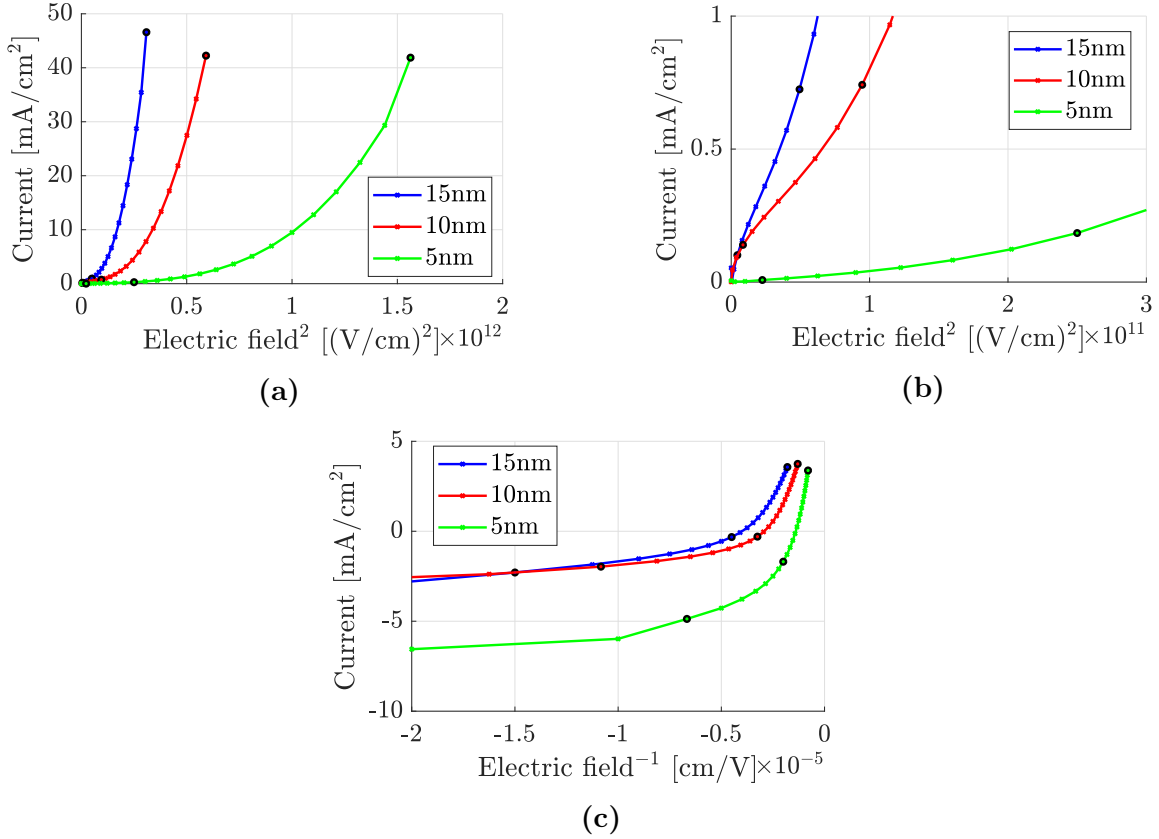
**Figure C.7:** CV hysteresis measurements of  $\text{WO}_3$  with an annealing at  $200^\circ\text{C}$  (a) and  $432^\circ\text{C}$  (b). The solid lines are for the measure at 1kHz and the dashed for 10kHz. The red indicates a measure negative to positive and the blue the opposite, positive to negative.

# D Additional data - IV

## D.1 Leakage mechanisms



**Figure D.1:** Electric field dependence for Space-charge limited (a) and the trap-assisted tunneling (TAT) (b) mechanism for the positive side of Figure 4.26. The black dots indicate the region between 0.2 to 0.7V.



**Figure D.2:** Electric field dependence for Space-charge limited (a), Space-charge limited zoomed (b) and the trap-assisted tunneling (TAT) (c) mechanism for the negative side of Figure 4.26. The black dots indicate the voltage at -0.1, -0.4 and -1V.

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