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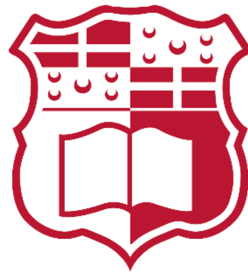

Production of amorphous silicon thin films using chemical vapour deposition

by

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ABSTRACT

Hydrogenated amorphous silicon thin films have been prepared using the Plasma Enhanced Chemical Vapor Deposition (13.56 MHz PECVD) technique over two kinds of substrate, boro-silicate glass and double-sided polished silicon wafers. The films were grown from a gas mixture of silane (SiH_4) gas and hydrogen (H_2). The content of hydrogen is a critical factor in hydrogenated amorphous silicon films due to the necessity to control the Staebler Wronski effect. In this study, the effect of deposition temperature and time over the film thickness and the content of bonding configurations of hydrogen in the film has been investigated. It was concluded that the thin films produced at higher temperatures have a larger concentration of bonded hydrogen, but this does not affect the topographical structure. It has also been proved that the thickness of the film increases with the deposition time.

Keywords: amorphous silicon, hydrogen content, PECVD, photovoltaics, solar cells, thin films.

NOMENCLATURE

SC	Solar Cells
P	Pressure (mbar)
T	Temperature (ºC)
t	Time (min)
SiH_4:H_2	Silane Hydrogen ratio
P_ρ	Power density (W/cm^2)
RF	Frequency (MHz)
d	Thickness (nm or µm)
Eg	Band Gap (eV)
α	Absorption coefficient (cm^{-1})
sccm	Standard cubic centimeters per minute
PECVD	Plasma Enhanced Chemical Deposition
FTIR	Fourier Transformed Spectroscopy
AFM	Atomic Force Microscopy
EMA	Effective Medium Approximation

1. INTRODUCTION

In the last past few years, the production of solar cells has grown. The most used and sold in the market nowadays are the crystalline silicon solar cells, this kind of SC corresponds to the first generation. The second-generation cells are also widely available, these are considered to be the thin films solar cells, which can have a significantly smaller thickness and can be made flexible. The material used as a substrate can be of any kind, including glass, plastic or metal. Different materials can be used as the photoactive media and these include, but not limited to cadmium telluride, Copper indium gallium diselenide, and more commonly amorphous silicon [1]. When comparing first generation and second generation solar cells, thin films present some advantages over crystalline solar cells. The production costs are lower, larger areas of solar cell can be achieved through vacuum or room temperature liquid processing and there are a large variety of substrates that can be used including transparent ones [2]. The conversion efficiency of the thin films solar cells is however limited, at the beginning (1975) it was practically zero, but with the years it has evolved, by 2009 the efficiency was of 9,5% nowadays efficiency of 13.5% can be reached. [3]

The first time amorphous-silicon (a-Si:H) was deposited onto a substrate using a silane glow discharge was in 1955 by Sterling in 1969 [2]. Chittick obtained the first intrinsic amorphous silicon of acceptable quality by plasma enhanced chemical vapor deposition PECVD [2]. While the PECVD technique is the most used nowadays, there are also other methods available on the market such as hot wire chemical deposition or very high-frequency chemical vapor deposition. All these processes have one thing in common, they use a relatively low deposition temperature (never exceeds the 600ºC), and the process normally is performed between 100ºC and 300ºC. There are many factors that during deposition affect the quality, thickness and other properties of the layers produced. The more salient of these are the temperature, pressure, plasma power, RF frequency, and gas flow- rate amongst others [4].

Amorphous silicon atoms do not form a well-ordinated crystal lattice, the atoms are bonded randomly, and because of that some atoms are not fully linked and have dangling bonds. These dangling bonds represent defects in the network and are understood to cause anomalous electrical behavior [1]. While examining amorphous silicon cells, Staebler and Wronski observed in 1977 [5] that photoconductivity and the dark conductivity of glow-discharge deposited amorphous silicon can be reduced by prolonged illumination with intense light, leading to a decrease in cell performance.

At the time it was hypothesized that this was due to metastable defects brought on by unterminated bonds which act as photo-electron sinks. Hydrogen, with its small atomic size and unitary charge can be very effective to passivate a large part of the dangling bonds and can be introduced as a gas precursor together silane in the PECVD chamber during processing. Hydrogen concentration and its complex bonding structure leads to metastable changes in the amorphous silicon and while limiting the effect, hydrogenated cells still suffer from the Staebler – Wronski effect.

More recently the need for higher efficiencies has made amorphous silicon thin films evolve into microcrystalline silicon (μc-Si:H). These coatings have better qualities and are a more stable absorber material than fully amorphous silicon. In order to obtain microcrystalline silicon, the hydrogen flow rate has to be increased considerably. This allows for a large amount of hydrogen to be incorporated during deposition, thus passivating most of the dangling bonds and promote structured growth. Thin film silicon solar cells with the highest efficiencies have been reported for films which have a medium to average crystallinity, where half of the volume of the cell is amorphous silicon and the other half is microcrystalline [6]. In such cells, a reduction of the Staebler Wronski effect was shown to be reduced considerably.

In this project, an investigation is done to determine the optimal operating parameters to produce hydrogenated amorphous silicon cells through plasma enhanced chemical vapor deposition through a set of experiments. Following this, deposition on pure crystalline silicon is conducted in order to find how the deposition time and temperature affect the amorphous silicon coatings properties, including thickness, content of hydrogen, band gap, spectral response and surface morphology.

1. METHODOLOGY, THEORY, AND CALCULATIONS

1.1 FABRICATION OF THE AMORPHOUS SILICON THIN FILMS

Amorphous silicon thin film solar cells were fabricated over two different substrates, boro-silicate glass and double-polished crystalline silicon. The thickness of the substrates was 200 μm and 297 μm respectively. The area of the boron glass was 4 cm^2, and the silicon samples were obtained from a circular silicon wafer of 50 mm diameter cleaved along the atomic plane into 4 quadrants.

Before the silane deposition, a cleaning procedure was carried out on both substrates. The boro-silicate glass substrates were cleaned in five consecutive steps. First, these were introduced individually in a glass beaker with distilled water and soap for five minutes in an ultrasonicator. Following washing with distilled water, the substrates were then introduced in distilled water for another five minutes.

Substrate	Nº	P (mbar)	T (ºC)	t (min)	$SiH_4:H_2$	Pρ (W/cm^2)	Distance (mm)	RF (MHz)
Boro-Silicate Samples	1	1	95	10	1:10	34	15	13,56
	2	1	200	10	1:10	17	15	13,56
	3	1	100	10	1:10	17	15	13,56
	4	1	100	10	1:10	17	15	13,56
	5	1	100	15	1:10	17	15	13,56
	6	1	100	15	1:10	17	15	13,56
	7	1	150	10	1:10	17	15	13,56
	8	1	150	15	1:10	17	15	13,56
Silicon Samples	1. a-Si:H	1	100	10	1:10	17	15	13,56
	2. a-Si:H	1	100	15	1:10	17	15	13,56
	3. a-Si:H	1	150	10	1:10	17	15	13,56
	4. a-Si:H	1	150	15	1:10	17	15	13,56
	5. a-Si:H	1	100	5	1:10	17	15	13,56
	6. a-Si:H	1	150	5	1:10	17	15	13,56
	7. a-Si:H	0,4	150	5	2:10	17	15	13,56

Table 1. Operational conditions of amorphous silicon deposition in the PECVD.

After this, they were washed with isopropanol and then introduced in a beaker filled with 99.9% isopropanol for another five minutes. Once this dipping procedure was finished the samples were dried with a lateral jet of nitrogen gas. The final step in the cleaning procedure was to immerse the substrates in a hydrogen plasma, so for this step, the samples were introduced in the chamber of the PECVD and immersed for 60s at the pressure of 0.4 mbar, a power density of 0.146 W/cm^2 and a flow of hydrogen of 10 sccm [7]. The silicon substrates were delivered with clean room handling certification and they did not require wet cleaning steps. Such substrates were handled in a glovebox and only pre-cleaned with the hydrogen plasma step just before deposition.

The initial hydrogenated amorphous silicon layers were deposited over the boron glass as a means for familiarization with the operation of the highly complex plasma enhanced chemical vapor deposition (PECVD) machine. Such layers were deposited with an excitation frequency of 13.56 MHz at a pressure of 1 mbar, a power density of 0.05 W and a distance between electrodes of 15 mm. The process gases were a mix of silane (SiH_4) and hydrogen (H_2). From previous experiments in the laboratory, it was known that the optimal silane to hydrogen flow rate was either 1:10 or 1:5, depending on other process conditions. In this case, the ratio used was 1:10, because when the silane is less diluted the particles are bigger. Two metallic holders were manufactured in order to steady the samples on the chamber`s supporting base. This ensured that the samples did not change position during the deposition process and were not displaced during the venting of the chamber to atmospheric pressure. After the boron glass deposition, the silicon samples were coated. Table 1 shows all the post-training parameters used for the deposition of the different layers.

1.2 MEASUREMENT OF THE FILM THICKNESS AND BAND GAP

Spectrometric ellipsometry is a technique which measures the change in phase of polarized light upon the light being transmitted or reflected by a sample, yielding values for reflection phase difference (Δ) and amplitude reduction ratio (ψ) and as shown in Figure 1. The obtained result is compared with a specifically built mathematical model in order to determine the specific spectral properties of the sample. [8] In this project ellipsometry has been used for the measurement of the thickness, surface roughness and the band gap of the produced coatings.

The measurements were carried out at room temperature. To fit the samples after the measurements, two simulation layers were used, the first one was EMA

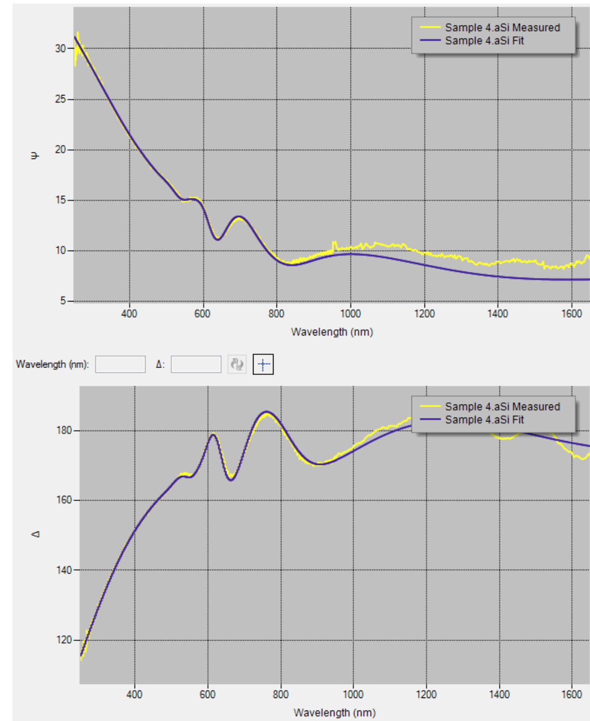


Figure 1. Psi Delta curves for sample 4. A-Si:H

to simulate the surface roughness and the second one followed dispersion laws. The two dispersion laws used were based on Tauc-Lorentz and Gauss formulae. The Tauc-Lorentz has also been used to model the dielectric function of the amorphous material or transparent conductive oxide. In general, this model is used for insulators, however it has allowed us to approximate the band gap energy of the material. Gauss models are typically used for amorphous materials or glasses [9] and were used to complement the full model.

The roughness values of the amorphous silicon were necessary to generate a dependable EMA layer model. These were measured through the use of atomic force microscopy (AFM) on an area of 0,25 μm^2 of every silicon sample.

As a means to validate the approach taken, two of the boron glass samples (3 and 6) were sent to the National Institute for Research and Development in Electrochemistry and Condensed Matter, which is a collaborating laboratory in Romania. The obtained thickness measurements showed good corroboration with what was determined at the Marsaxlokk laboratories

Confirming an exploratory study by a preceding team working at the laboratories, the thickness of the coating increases quasi-linearly with deposition time independently from the processing conditions.

1.3 MEASUREMENT OF THE CONCENTRATION OF HYDROGEN

Fourier transformed infrared spectrometry (FTIR) was used to determinate the amount of bonding configurations of hydrogen contained in the double side polished silicon samples, using a plain silicon substrate as a reference, at a wavelength range of 400-5000 cm^{-1}. The measurements were carried out at room temperature and atmospheric pressure.

It was noted that due to matching absorption lines, the presence of carbon dioxide and water caused many interferences while conducting the measurements. In order to reduce the concentration of carbon dioxide and keep the amount of water vapour stable, the chamber was purged with nitrogen for a defined period between every measurement. Due to very strong absorption of SiO_2 at the wavelengths of interest, only the samples that had silicon as a substrate were measured successfully

The absorption coefficients were calculated from the transmission using Equation 1, this is the Brodsky method [10], [11].

$$T_{film} = \frac{4T_o^2 * e^{-\alpha d}}{(1+T_o)^2 - (1-T_o)^2 * e^{-2\alpha d}} \quad \text{Eq. 1}$$

Where T_{film} is the transmission of the film, T_o the theoretical transmission of the silicon substrate and has a value of T_o=0,54 cm^{-1}, α is the absorption coefficient and d is the thickness of the amorphous silicon layer.

The transmission of each sample is shown in figure 2, the green curve represents the sample of pure silicon with an unpurged chamber where the absorption of the carbon dioxide can be appreciated. Carbon dioxide presents bending mode at the frequency of 650 cm^{-1}, asymmetric mode at 2340 cm^{-1}, and also present symmetric at 1330 cm^{-1} but this mode does not produce any changes in the transmission because the infrared does not make any changes in the dipolar moment. It also generates interferences at the frequency between 3550-3750 cm^{-1} but the amorphous silicon does not have any appreciable absorption at this frequency [12] so it was not of any particular concern. For the graphic to be clearer the wavelengths represented are only from of 380 to 2500 cm^{-1} as there were no response in the rest of frequencies.

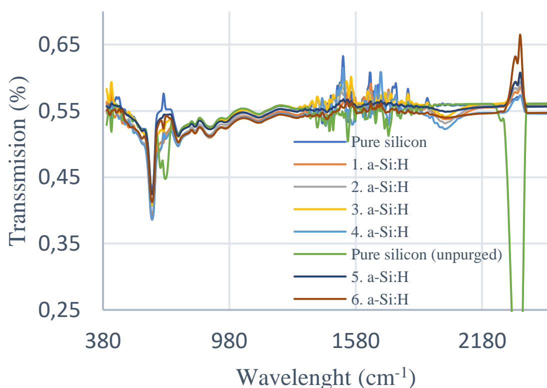


Figure 2. Transmission vs Wavelength

Contact angle measurements were made in order to get an idea of the content of hydrogen in the different silicon samples. Theoretically, the dangling bonds of the unpassivated pure silicon will attract more water than the hydrogenated amorphous silicon, so the contact angles on the water drop should be larger in the double side polished silicon than in the amorphous silicon.

2. RESULTS AND DISCUSSION

Three separate ellipsometry measurements were done in different parts of the samples in order to confirm that the coating was uniform. As shown in table 2 the results of the measurements that were fitted with the Tauc-Lorentz and Gauss models and yielded the best R^2 values are shown. The first two boron glass samples showed several inconsistencies and ellipsometric results were not fitted successfully.

Sample	T (ºC)	Time (min)	Thickness (nm)	Eg (eV)
3	100	10	81,048	1,63752
4	100	10	78,936	1,6
5	100	15	134,304	1,68315
6	100	15	132,455	1,67518
7	150	10	139,834	1,63009
8	150	15	226,175	1,65644
1. a-Si:H	100	10	89,194	1,66
2. a-Si:H	100	15	189,507	1,63424
3. a-Si:H	150	10	106,579	1,77513
4. a-Si:H	150	15	211,019	1,665
5. a-Si:H	100	5	37,357	1,69636
6. a-Si:H	150	5	94,985	1,65
7. a-Si:H	100	5	19,73	1,78491

Table 2. Results obtained from the ellipsometry measurement (Film thickness and band gap)

As expected from previous studies the thickness of the samples increases with the deposition time, it can be seen in Figure 3 the evolution of the thickness when increasing the time in two different temperatures. The results of the sample number three and six were compared with results obtained from a collaborating laboratory which was equipped with a goniometer- type ellipsometer which could do measurements at different analyzing angles. The thickness obtained for the two samples were 82nm and 125nm nm respectively, which at 81.05nm and 132 nm, are equivalent to the ones obtained in house. On the other hand, the values obtained for the band gap are 1.755 and 1.72 eV, in this

case the error is bigger, with 6.7% being for the first sample and 2.6% for the second.

Sample 7. a-Si:H was produced at a lower pressure of 0.4 mbar; from literature, a thinner coating is expected. This is because while energized the plasma is unstable at this pressure conditions resulting in the relative pressure of hydrogen to slowly increase while the relative pressure of silane to slowly decrease. This is caused by an increase in silane depletion at higher total pressures, which results from a higher power dissipation by the electrons [13]. This phenomenon was confirmed and a thickness of only 19.7 nm was obtained for otherwise equivalent process conditions.

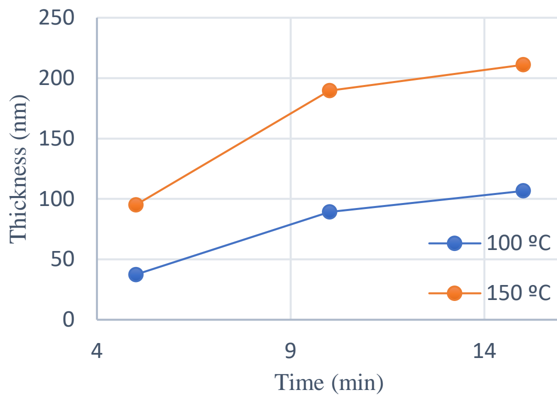
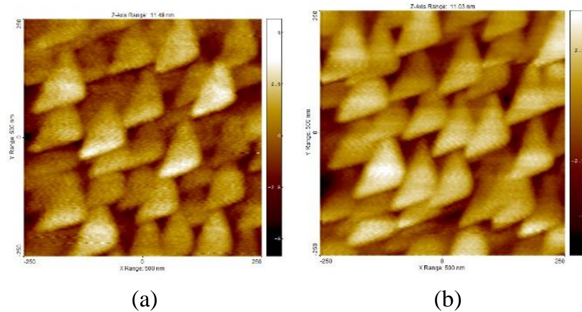


Figure 3. Effect of time over the film thickness in the samples coated over silicon.

The measurement of the roughness with the AFM demonstrates that the EMA layer is approximately of 3 nm, this value differs between the different samples. With this technique it can also be seen that the amorphous silicon structure does not vary with the time or the deposition temperature and crystalline formations in the form of triangular shapes are observed. Figure 4 shows the surface of the two samples coated over silicon for 150 ºC, sample number 3. a-Si:H and 4. a-Si:H.



(a) (b)

Figure 4. The surface crystallinity of the samples (a) 3. a-Si:H and (b) 4. a-Si:H

From ellipsometric measurements, it was determined that the index of refraction presents a maximum at a wavelength of 450 nm for all the samples. Samples made with lower deposition time have a general index of refraction which is lower than the ones made in longer times.

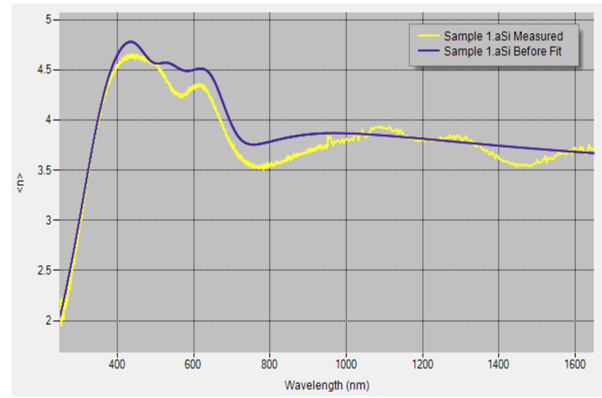


Figure 5. Index refraction vs Wavelength of sample 1. a-Si:H

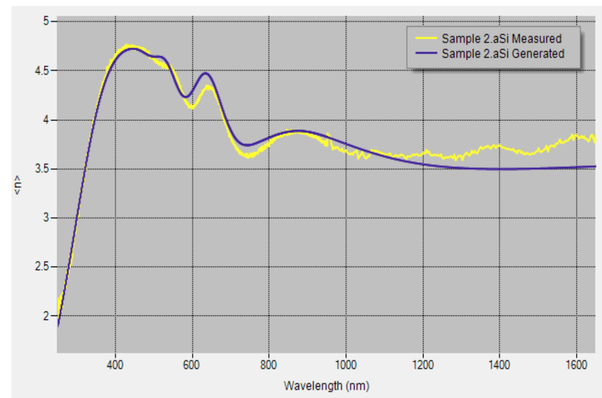


Figure 6. Index refraction vs Wavelength of sample 1. a-Si:H

From the measurements of the FTIR the graphs of the transmission vs electromagnetic frequency were obtained. The absorbance coefficient has been evaluated for the wavelength frequency infrared spectra from 570 to 720 cm^{-1} using the Brodsky method. From Literature it was known that crystalline silicon absorbs infrared at 615 cm^{-1}, which peak is also observed in Figure 1. This absorbance frequency peak can potentially present a deconvolution problem and unless the sample and the silicon reference are perfectly matched it would interfere with the hydrogenated amorphous silicon peak measurements [11].

In Figures 7, 8 and 9 the absorption coefficient vs. frequency the are shown, where it can be observed that the absorption amplitude in the region of 520-720 cm^{-1} decreases when increasing the process temperature. From different literature it is known that the concentration of total hydrogen in the films depends on the absorption concentration [14], [15], but there are no studies that correlates the amount of bonded hydrogen to the absorption [16]. In the graphs (5, 10 and 15 min deposition time) it can be observed that the experiments behave the same way as the papers describe, where in all the cases the absorption coefficient increases with the temperature. It is known that an increase of the temperature during the deposition of the film leads to a decrease in the content of hydrogen due to the decreased

of the clustered hydrogen, and also to a variation in the silicon-hydrogen vibrational modes in the amorphous silicon thin films.

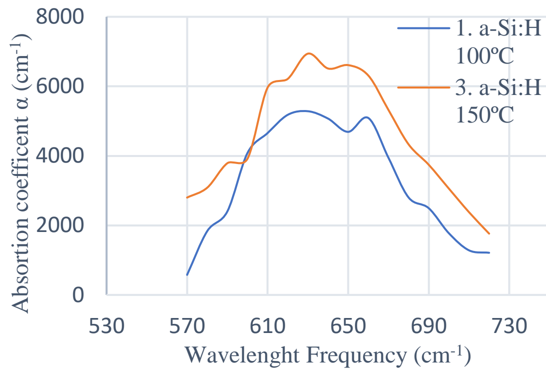


Figure 7. Infrared absorption spectra of a-Si:H films deposited at 100 and 150 ºC and 10 minutes in the wagging–rocking mode region.

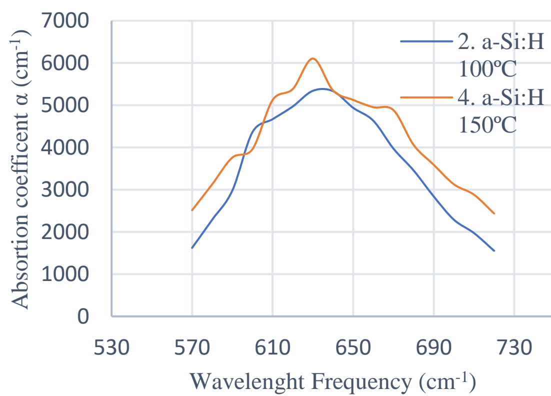


Figure 8. Infrared absorption spectra of a-Si:H films deposited at 100 and 150 ºC and 15 minutes in the wagging–rocking mode region.

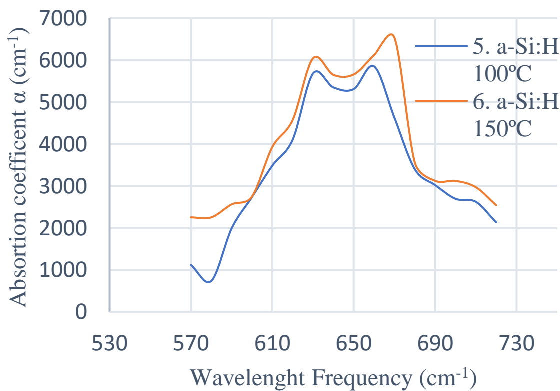


Figure 9. Infrared absorption spectra of a-Si:H films deposited at 100 and 150 ºC and 5 minutes in the wagging–rocking mode region

The next mode found in the literature review is the bending and scissoring mode in 840, 850 and 880 cm^{-1}. In this experiment none of this peaks have been found in the FTIR measurements, this peaks are associated with the dihydrides (SiH_2) scissoring mode and the polysilanes ($(SiH_2)_n$) which are usually undesired in good quality coatings.

The study of the hydrogen bonding configuration has led to a new peak, it is located at 2000 cm^{-1}, this peak corresponds to the isolated monohydrides (SiH) in the bulk, they are created by the saturation of the dangling bonds during the deposition of the film. From literature review it is known that there must be another peak around 2100 cm^{-1}, this peak corresponds to the polyhydride silicon or the clustered monohydride groups on the inner surface of microvoids. In the experiments carried out in the laboratory this peak in not seen, this means that the bonds formed between the silicon and the hydrogen are monohydres, so it means that the layers obtained are of high quality and have good potential for future thin solar cells.

3. CONCLUSIONS

Amorphous silicon thin films were produced by PECVD at different temperatures and deposition times in order to study the effect of these parameters on the thickness, crystallinity and the hydrogenation. A complement of techniques was used to measure the produced films, including transmission FTIR, Spectroscopic ellipsometry, Contact angle measurement and atomic force microscopy. It can be concluded that an increase in the deposition time leads to a thicker a-Si:H coating. The different vibrational molecules modes indicate the presence of hydrogen in the coating. At higher deposition temperatures the absorbance coefficient is higher, this means that the total amount of hydrogen in the film is lower than the films fabricated at lower temperatures. It was also shown that with a well determined parameter set and temporally controlled processing, good quality films which are free from dihydrides and their complexes can be produced. This paves the way for the production of highly efficient fully functioning thin film solar cells with potentially limited light induced degradation.

4. FURTHER WORK

In order to obtain better fittings in the ellipsometry, different models will be tried over the silicon samples. Grazing Incidence X-ray diffraction (GIXRD) is used to study surfaces of layers so it will be used to measure the microcrystallinity of the silicon samples. Measurement of the photoluminescence and electron life time at different light exposure times will be done over the samples.

The deposition process will be repeated with the introduction of dopant gases such as Diborane (B_2H_6) and Phosphine (PH_3) in order to produce an efeective

P/N junction that yields a working thin film PV cell with controllable microcrystallnity.

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