

On the Reproducibility of a-Si:H Deposited with an Expanding Thermal Plasma

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Abstract---Expanding Thermal Plasma chemical vapor deposition (ETP-CVD) is a relatively new technique that is very promising for fast deposition of, among others, hydrogenated amorphous silicon, compared to conventional radio frequency plasma enhanced chemical vapor deposition. When a new set-up is used to develop a material, reproducibility is often an issue and the influence of standard parameters, such as temperature, pressure or process gas flows, can be affected by at that moment unknown parameters. We identified parameters that strongly influenced the material properties, such as the number of plates in the arc and reduction of the channel diameter. In more detail, the density of the material, as well as the hydrogen content have been monitored using Fourier transform infra-red spectroscopy and it was shown that a large helium back flow from the yoke was necessary to control the sample temperature.

In this article, we present the thorough study that has been carried out to improve the reproducibility of the ETP set-up and the deposition technique. This study led to a better control of, in particular, the sample temperature and to the reproducibility of a-Si:H thin films.

Keywords---Reproducibility, hydrogenated amorphous silicon, ETP-CVD

I. INTRODUCTION

Originally, the Expanding Thermal Plasma (ETP) technique was developed by the plasma group of the Eindhoven University of Technology (TU/e) in order to study plasma chemistry. A characteristic feature of this ETP technique is the so-called remote plasma, which permits plasma study at a different position from where it is generated. It appeared that the ETP method was suitable for the deposition of hydrogenated amorphous silicon (a-Si:H) and thus could be used for the fabrication of thin-film solar cells. Since 1999, the solar cell group of the Delft University of Technology (TUD), in partnership with the TU/e, has acquired an ETP set-up. The first results were promising and solar cells with an

efficiency above 4% could be initially fabricated. However, it appeared that the reproducibility of the layers, so consequently of the solar cells, deposited at the TUD varied over time.

In the ETP technique, the plasma production takes place remotely. This means that the creation of the plasma, the transport and the deposition are happening separately in different parts of the set-up. The main two parts of the ETP set-up are the high-pressure plasma source, the so-called cascaded arc, and the low-pressure deposition chamber. The plasma source consists of six copper plates with a 2.5-mm diameter orifice in the center, forming a channel for the arc discharge. The plates are electrically insulated from each other by boron-nitride discs and O-rings, and they are water cooled. The plasma is created between three cathodes, positioned symmetrically at the top of the arc, and the grounded anode copper plate at the bottom of the arc (Fig. 1). Non-depositing gases, such as argon and hydrogen, are used to create the plasma in the arc and the discharge is controlled by the current (usually 40 A). The power dissipated in the arc is typically 5 to 8 kW.

The plasma emanates from the high-pressure cascaded arc (~0.5 bar) through a nozzle and expands into the deposition chamber, which is at a pressure of typically 0.2 mbar. Due to the large difference in pressure between the arc and the chamber, the plasma is accelerated leading to a supersonic expansion. At a few centimeters from the arc outlet there is a stationary shock, after which the plasma expands sub-sonically. The reactive ionic and atomic species, such as Ar⁺ and H emanating from the arc have typically a velocity after the shock of 1000 m/s, which slowly decreases to zero at the stagnation point.

The reaction chamber has a length of 72 cm and a diameter of 33 cm. The precursor gas (silane) is injected through a ring located at 4.5 cm from the cascaded arc outlet and the distance from the source to the substrate holder is 43 cm. During processing the system is pumped

II. EXPERIMENTAL DETAILS

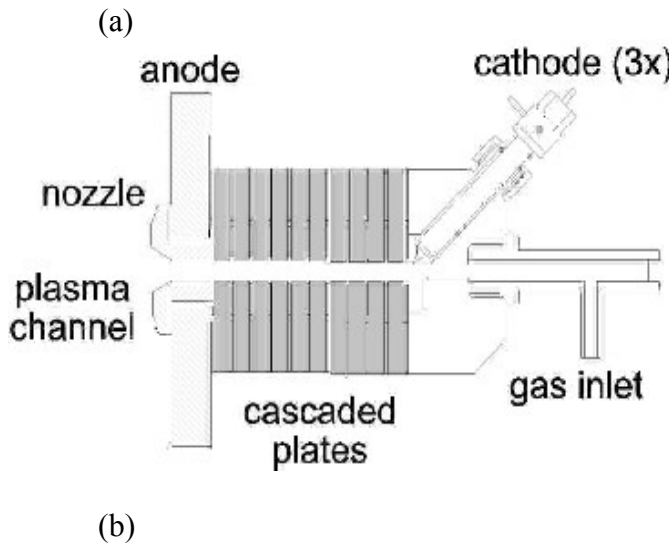
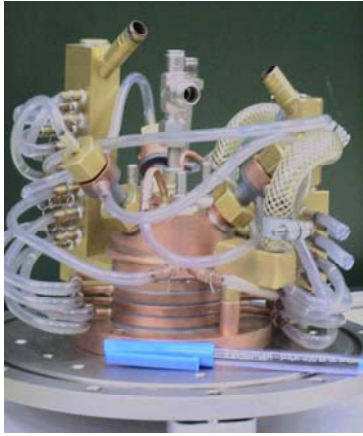


Figure 1: Cascade arc, plasma source of the ETP set-up (a) picture, (b) schematic drawing.

by a stack of roots blowers (pumping capacity $500 \text{ m}^3/\text{h}$), and overnight it is pumped by a turbo pump reaching a base-pressure of $\sim 10^{-6}$ mbar. For more details on the set-up, see reference [1].

In this paper, we present the influence of several parameters on the quality of a-Si:H thin films and our action to control these. In the first part, the experimental details are exposed, presenting the reference deposition conditions, the experimental procedure followed and indicating the characterization methods used. In the result part, we show the influence of unusual parameters on the performance of the ETP, such as the number of plates in the arc, we develop the analysis on the substrate temperature control, varying the He back flow, the heating time before deposition and the substrate temperature. Finally we show in a reproducibility study that the opto-electronic properties of a-Si:H thin films deposited with the ETP technique are reproducible with a standard deviation of 5%.

In order to keep track of the performances of the ETP set-up, a reference layer is regularly deposited to check both its properties and the conditions of the whole system. The gas flows used are 600 sccm of Ar, 200 sccm of H_2 and 200 sccm of SiH_4 . The deposition temperature is kept fixed at 250°C . The current through the arc is 40 A, the typical voltage obtained across the arc is 160 V and the pressure in the arc between 0.41 and 0.43 mbar. The reference sample is deposited at a rate between 0.7 and 0.9 nm/s.

The a-Si:H thin films are deposited on Corning glass and crystalline silicon substrates. They were cleaned following a procedure, which consists in 10 min. cleaning in ultrasonic acetone bath to remove all fat substances and particles, then 10 min. in ultrasonic isopropanol (IPA) bath to rinse the substrates, and finally dry out under a nitrogen flow to avoid that any trace of IPA remains on the sample.

During the growth of a-Si:H thin films, some deposition occurs not only on the substrate but also on the walls and windows of the reactor. In order to limit out-gassing from the walls and avoid contamination, an Ar plasma is run with CF_4 injected directly in the reactor to etch the silicon away. After this cleaning run, a mixture of Ar and H_2 is used to condition the reactor. Finally, a dummy and reference layers are deposited to check that the conditions are back to our reference level.

The samples deposited on Corning glass are used to perform Reflection-Transmission measurements to determine the thickness of the layer and the optical properties, such as the refractive index, n_{RT} , and the optical band gap, E_{Tauc} . The latter is obtained following Tauc expression [2]. Dual Beam Photoconductivity (DBP) is carried out in order to determine the sub-bandgap absorption, which is correlated to the density of states distribution in the mobility gap. The Urbach energy, E_U , is the characteristic energy of the exponential slope of the absorption spectrum. Light and dark conductivity measurements are also carried out on these samples. Fourier Transform Infra-Red (FTIR) spectroscopy is performed on the films deposited on crystalline substrates to determine the hydrogen content, c_H , from the wagging mode at 640 cm^{-1} , and the hydrogen content of the low and high stretching modes, c_{LSM} and c_{HSM} , at respectively 2000 cm^{-1} and 2100 cm^{-1} . These parameters give information on the structure of the material. The microstructure factor R^* is defined as $R^* = I_{HSM}/(I_{HSM}+I_{LSM})$ where I_{HSM} and I_{LSM} correspond to the integrated absorption strength of the HSM and LSM respectively. The mass density $\rho_{a-Si:H}$ of the thin films is determined according to the Clausius-Mossotti equation [3].

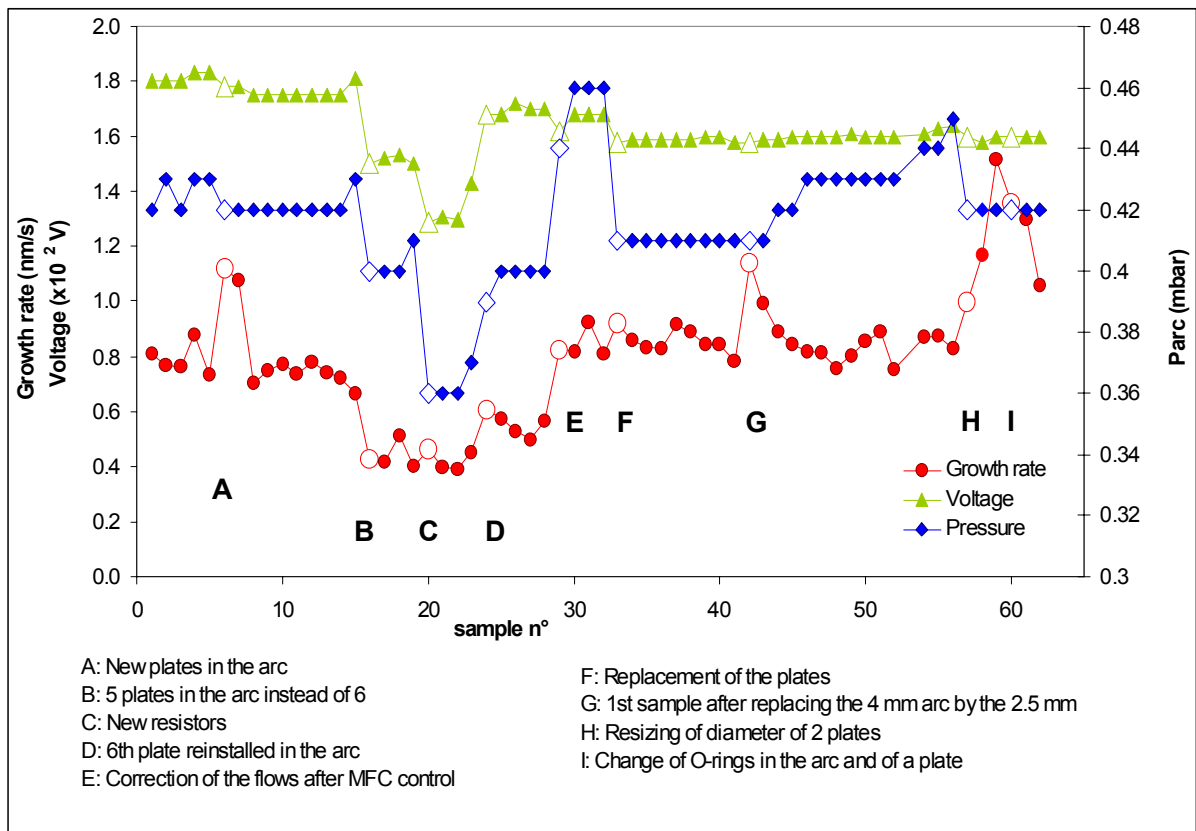


Figure 2: History of the reference layer deposition conditions: growth rate, voltage and pressure in the arc.

III. RESULTS

A. Deposition history

We monitored the growth rate, the voltage and the pressure in the arc. Figure 2 shows the history of the deposited layers before the reproducibility study.

From figure 2, it is clear that several parameters influence the ETP set-up. First of all, we can see that the number of plates forming the arc determines the voltage across the arc. As the voltage was going up, a plate was removed from the arc (case B), but then not only the voltage but also the growth rate decreased. We can see that putting back the 6th plate (case D), as well as correcting the gas flows for deviation of the mass flow controllers (case E), permitted to obtain the standard conditions for our reference settings, namely a growth rate between 0.7 and 0.9 nm/s, a pressure in the arc between 0.41 and 0.43 bar and a voltage around 160 V. When the pressure increased again because some extreme settings were tested (e.g., very high H₂ flows), the arc was dismantled and cleaned, or some parts were changed (cases F and H) and the pressure returned within the standard range. Thus a large pressure increase in the arc is a sign of deterioration of the copper plates, indicating that the inner diameter might have been reduced due to sparking and local melting of the copper.

Secondly, when new plates are built in the arc, either because they are dirty or deteriorated (cases A, F and H), or because another arc was used in the meantime (case G), it can be seen that the reference pressure in and the reference voltage across the arc are obtained again. However, the growth rate increases and a dummy should be carried out before processing after the arc has been opened. We think indeed that oxygen could be trapped in the arc and a dummy is necessary to 'clean it out'. The increase in growth rate can be due to the growth of less dense material, the particle flux reaching the substrate surface remaining the same.

Finally, it can be noticed that the implementation of extra resistors to sustain the power of the arc for the deposition of microcrystalline silicon (case C) decreased the voltage and the pressure in the arc. This changed our reference voltage from 180 V to 160 V.

In summary, the number of copper plates forming the arc is important as it determines the voltage across the arc when the plasma is on. We found that, when the voltage increased, removing a plate in order to reduce it was not a good solution, as the growth rate will decrease. Moreover, the increase in voltage is due to a deterioration of the plates. This can happen when extreme conditions are used (high H₂ flows) and the arc starts to spark. The inner diameter of the arc channel is

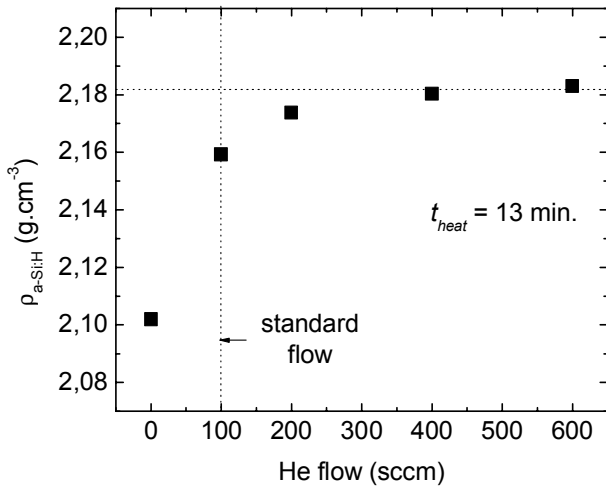


Figure 3: Mass density of a-Si:H thin films versus Φ_{He} .

reduced by some melted copper, and in these conditions the plasma is less stable. The diameter of the boron-nitride discs that separate the copper plates should be just bigger than the channel diameter to perfectly insulate one plate from the other. The discs used had an inner diameter of 4.5 mm and their replacement by discs of 3-mm inner diameter permitted to achieve stable plasma. The position of the three cathodes in the housing is also influencing the voltage in the arc. One should take care that the three tips are positioned symmetrically in the orifice to avoid overloading of one of the cathodes. Moreover, these tungsten cathode tips can erode, although it is a quite slow process, and this influences the stability of the plasma. Finally, the copper plates should be scratches-free, as a tiny mark on the plate can lead to some air leak in the system, deteriorating the properties of the grown material.

Some parameters, which are not ETP-related, were found to have their importance for a good reproducibility of the a-Si:H layers. It is indeed essential to control all hard-ware, such as the gas mass flow controllers that can deviate from their set-point, the purity of the gases (purifiers have been installed on the SiH₄ and H₂ lines, 6.0 instead of 4.5), the pressure sensors that need to be regularly calibrated and the cleanliness of the substrates.

B. Temperature control

Before deposition, the sample needs to be heated up to the deposition temperature. It was shown before that 10 to 15 min. heating time were sufficient to do so when a He back flow was used [4]. However, we will show that temperature control, before and during deposition plays a tremendous role in the reproducibility of the layers properties. It is also important to let the sample cool down for a while in the load-lock before exposing it to the air, otherwise it undergoes a temperature shock, which can result in a strained layer.

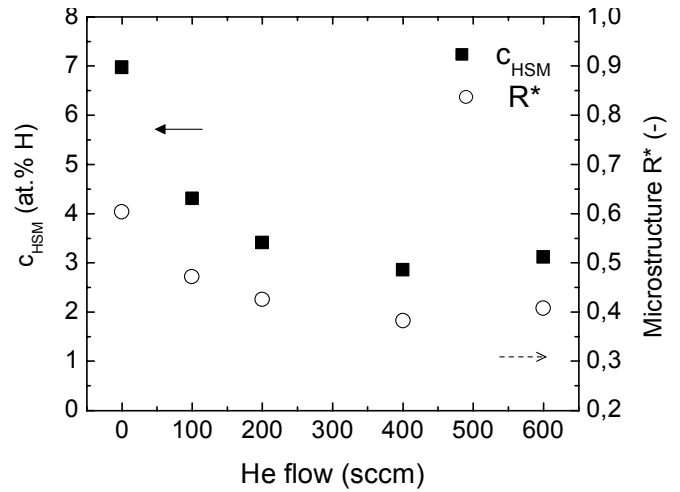


Figure 4: Hydrogen content from the high stretching mode and microstructure R^* versus Φ_{He} .

In order to control the temperature of the substrate before and during deposition, a study using FTIR spectroscopy was carried out. Three parameters were varied: the He back flow, Φ_{He} , the heating time, t_{heat} , and the substrate temperature T_{sub} . Applying a He back flow permits to convect the heat from the hot yoke to the sample and so to maintain the sample at the desired temperature. t_{heat} is referring to the time between the loading of the sample on the substrate holder and the beginning of the deposition when the shutter is removed from above the sample. The deposition temperature is kept at 250°C. The films have a thickness of 600 nm.

In the first experiment, Φ_{He} is varied between 0 and 600 sccm and t_{heat} is taken at 13 minutes. For this condition, the growth rate remains constant, independent of Φ_{He} . However, as shown in figure 3, the density of the a-Si:H thin film increases with higher He flows to saturate around $\Phi_{He} = 400$ sccm. The hydrogen content, as determined from FTIR, decreases as a function of He flow and reaches saturation for $\Phi_{He} \approx 400$ sccm. Moreover, the hydrogen content in the high stretching mode (c_{HSM}), as well as the microstructure R^* , follows the same decreasing trend (fig. 4). The c_{HSM} corresponds to hydrogen bonded at the surface of small voids [5], which indicates that the material densifies due to a lower micro-void concentration in the film. The drop of the R^* is also interesting as a lower R^* value generally indicates that the material is less sensitive to the Staebler-Wronski effect during degradation [6-8]. In summary, we conclude that the temperature of the a-Si:H growth surface is better controlled when a high He back flow is used.

For $\Phi_{He} \geq 400$ sccm, the low hydrogen content (~ 10 at.%) in the thin films indicates that the growing surface is sufficiently heated and that cross-linking and

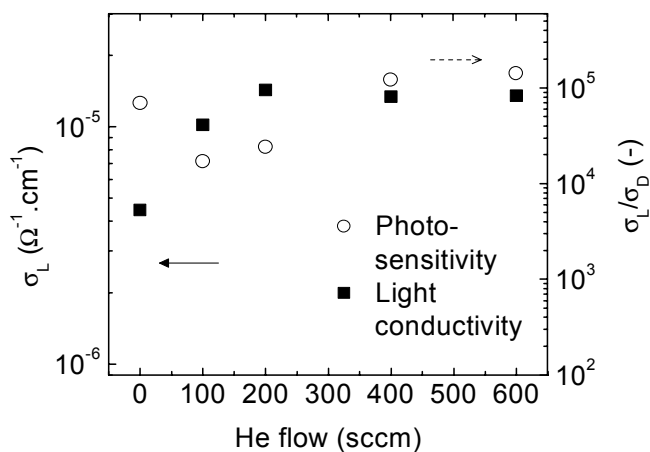


Figure 5: σ_L and photo-sensitivity of a-Si:H thin films versus He back flow, Φ_{He} .

elimination of H_2 can take place. The optical band gap decreases from 1.80 eV at $\Phi_{He}=0$ to 1.74 eV at 600 sccm. The light conductivity is also improved and as the dark conductivity decreases slightly, the photosensitivity of the thin films is enhanced for $\Phi_{He} \geq 400$ sccm (Fig. 5).

In a second experiment, the influence of t_{heat} is studied and the Φ_{He} is kept constant at 100 sccm. The growth rate is not affected by t_{heat} . However, as shown in figure 6, a heating time of at least 10 min. is necessary to obtain dense material. The c_{HSM} also decreases when more time is allowed to heat up the substrate, but even after 23 min. the low c_{HSM} obtained using $\Phi_{He}=600$ sccm is not reached (Fig. 7). The same trend is observed for the microstructure R^* . A lower micro-void density is incorporated in the material when a large heating time is used, but still the level is higher than for conditions with a high He flow. This means that it is preferred to heat up the sample using a high Φ_{He} than to wait a long time for

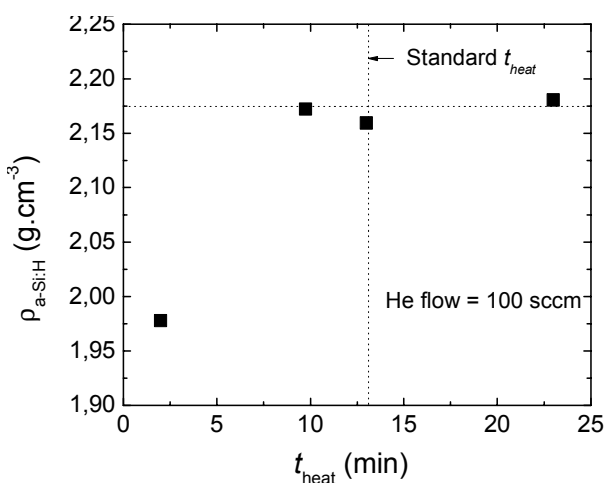


Figure 6: Mass density of a-Si:H versus heating time t_{heat} .

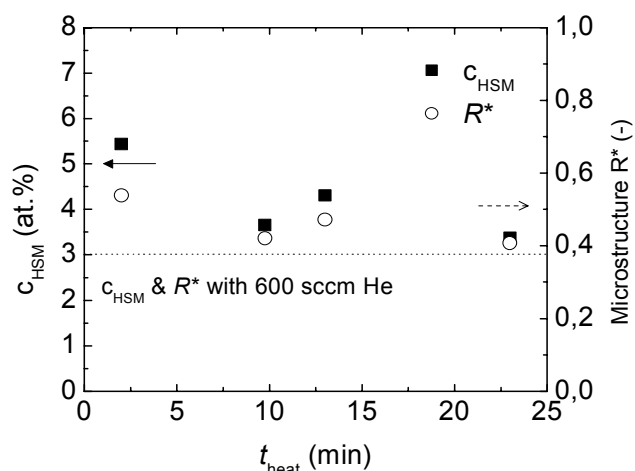


Figure 7: Hydrogen content from the high stretching mode and microstructure R^* versus t_{heat} .

the substrate to reach the desired temperature with a low Φ_{He} . The light conductivity is more or less constant with t_{heat} , with the best value at $1 \times 10^{-5} \Omega^{-1}.cm^{-1}$ for 13 min. heating time (Fig. 8).

In the third experiment, we varied the substrate temperature from 100°C to 400°C. Φ_{He} was set at 100 sccm and t_{heat} at 13 min. The density of the thin films increases with higher T_{sub} and the hydrogen content decreases below 10 at.% (Fig. 9.a & 9.b). Parallel to the decrease of c_{HSM} , the H content from the low stretching mode (c_{LSM}) increases. This means that more mono- or divacancies, with only Si-H bondings at their surface, are incorporated in the films instead of micro-voids. The R^* value drops below 0.2 at 400°C; this value could not be obtained either with a high Φ_{He} or a long t_{heat} . The a-Si:H network contains less defects, which is confirmed by the electronic properties of the material (Fig. 9.c), where the light conductivity goes from 1×10^{-7} to $2 \times 10^{-5} \Omega^{-1}.cm^{-1}$.

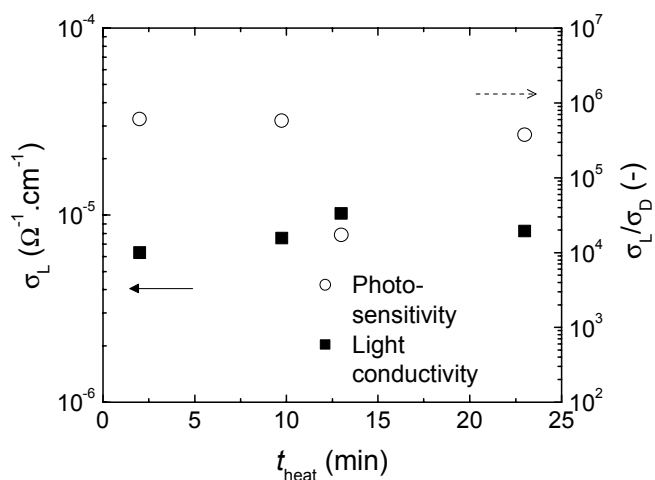


Figure 8: Light conductivity σ_L and photo-sensitivity of a-Si:H thin films versus t_{heat} .

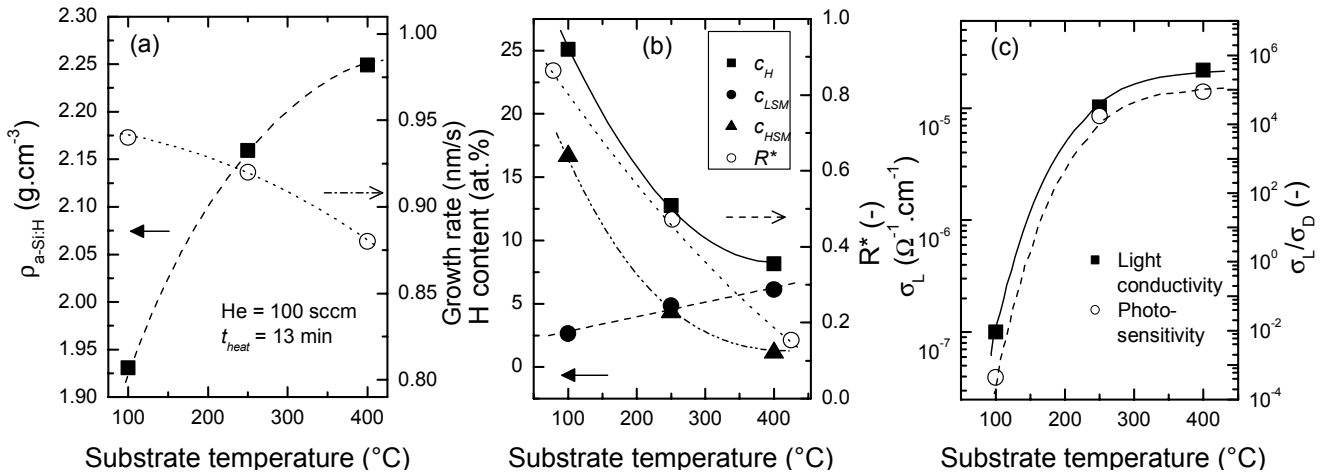


Figure 9: Mass density and growth rate (a), H content and microstructure, R^* , from FTIR (b) and light conductivity and photosensitivity (c) of ETP a-Si:H versus T_{sub} . Lines are guide to the eye.

In conclusion, the conditions used to prepare the sample before deposition so far (100 sccm He back flow for 10 min.) were not sufficient to bring the substrate to a stabilized temperature.

A He flow of 400 sccm has to be used for at least 13 min. to ensure that the growing surface is at the good temperature and stays at this temperature during the whole deposition. Higher He flows are not necessary as the properties of the a-Si:H thin films do not change for flows above 400 sccm. It is also not necessary to prolong the heating time further than 13 min. as very long t_{heat} would be needed to improve further the properties. To obtain denser material, closer to the density of c-Si, a higher substrate temperature can be used.

C. Reproducibility study

In order to estimate the effect of the measures taken to improve the control of the a-Si:H deposition with ETP, a reproducibility study on single layers has been carried out. The conditions were as follows: Ar = 900 sccm, H₂ = 200 sccm, SiH₄ = 200 sccm and He back flow Φ_{He} = 400 sccm; $p_{reactor}$ = 0.24 mbar and T_{sub} = 400°C. The current through the arc was 40 A, the voltage 150 V and the pressure in the arc 0.52 bar.

The growth rate, R_d , the refractive index at 1.96 eV, n_{RT} , and the Tauc optical band gap, E_{Tauc} , were determined. The normalised value to the average of these parameters can be found in figure 10. Their standard deviation is as follows: 3.8% for R_d , 1.0% for n_{RT} and 0.9% for E_{Tauc} . These parameters reproduce within a standard deviation of 5%. The electric properties such as the activation energy, E_{act} , and the Urbach energy, E_U , are plotted in figure 11. Their standard deviation is slightly higher, with respectively 3.9% for E_{act} and 5.9% for E_U . The higher standard deviation obtained for the E_U originates from the inaccuracy of the DBP fitting.

The dark and light conductivities vary less than an order of magnitude (Fig. 12). Note that the dark conductivity depends exponentially on the Fermi level position, and therefore a slight variation in the activation energy already implies a substantial change in σ_D . The light conductivity depends on the light generated carrier density in the material and their lifetime, and thus on the defect density.

From FTIR spectroscopy, c_H , c_{LSM} and $\rho_{a-Si:H}$ of the thin films have been determined (Fig. 13). $\rho_{a-Si:H}$ is reproduced very accurately with a standard deviation of 0.1%. c_H and c_{LSM} deviate somewhat more with a standard deviation of respectively 7.7% and 4.2%. This higher standard deviation is due to the inaccuracy of the background subtraction while analyzing the FTIR data for samples with a low c_H (6 at.%).

The average values of the electric-optical properties of the a-Si:H are listed in table I.

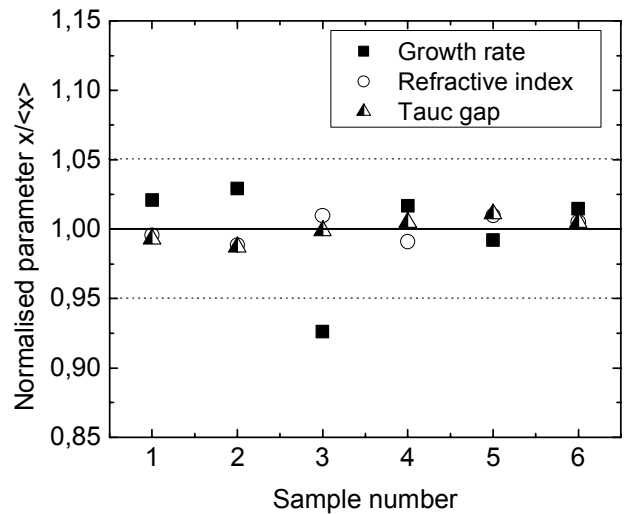


Figure 10: Normalized R_d , n_{RT} and E_{Tauc} values determined from RT measurements.

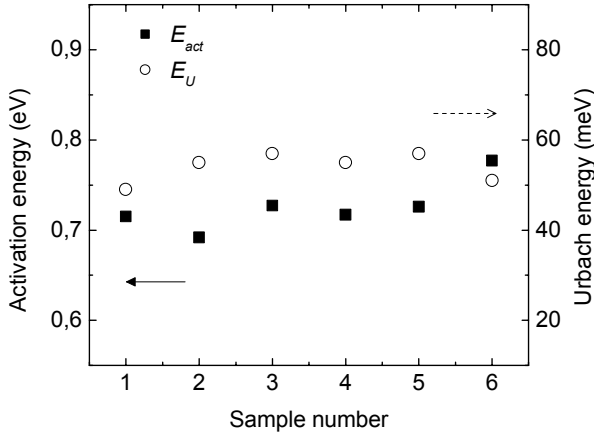


Figure 11: Activation energy and Urbach energy versus sample number.

IV. CONCLUSION

To ensure the reproducibility of layers grown with the ETP technique, the arc source of the plasma has to be checked and cleaned regularly. By monitoring the pressure in the arc, as well as the voltage across the arc, it is possible to get easily information about the status of the arc. An increase of these parameters is a sign of deterioration of the arc, which can be due to erosion of the tungsten cathode tips or to a diminution of the channel diameter if some sparks were observed from the arc.

Table I: Average of the main parameters of a-Si:H samples and their standard deviation.

R_d (nm/s)	1.93 ± 0.07	$\rho_{a-Si:H}$ (g.cm ⁻³)	2.25 ± 0.01
n_{RT} (at 2 eV)	4.23 ± 0.04	c_H (at.%)	5.9 ± 0.5
E_{Tauc} (eV)	1.67 ± 0.01	c_{LSM} (at.%)	4.6 ± 0.2
E_{act} (eV)	0.73 ± 0.03	R^* (-)	0.05 ± 0.03
E_U (meV)	53.9 ± 3.2		

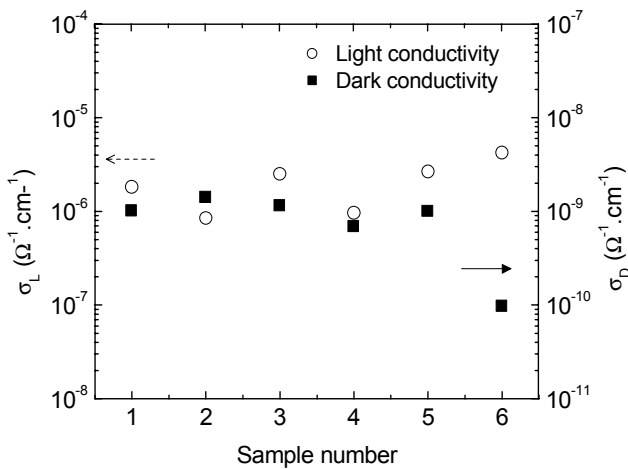


Figure 12: Light and dark conductivity versus sample number.

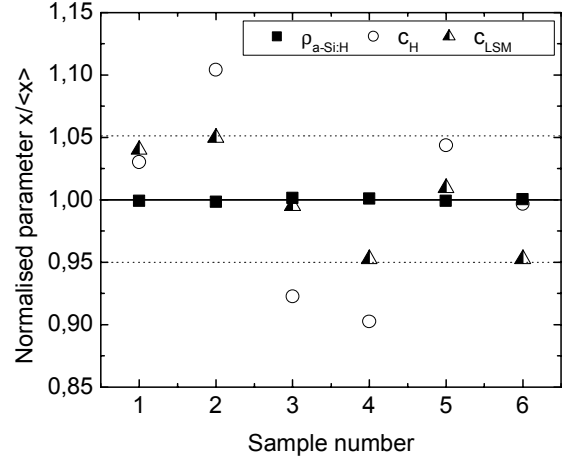


Figure 13: Normalized $\rho_{a-Si:H}$ and c_H values determined from FTIR measurements.

Another important issue concerning the reproducibility of a-Si:H is the temperature control of the substrate and thus of the growing surface. Before deposition, a heating time of at least 13 min. with a He back flow of 400 sccm should be allowed to bring the substrate at the desired temperature. During deposition, the same He flow should be used to maintain the temperature and avoid that the substrate heats up further because of the direct exposition to the plasma beam.

Finally, when these precautions are taken, the a-Si:H thin films deposited by ETP-CVD are reproducible. A variation of less than 5% is found for parameters such as growth rate and mass density, whereas the variation in the Urbach energy is lower than 6%. The electric properties of the material are more difficult to reproduce as they depend exponentially on the position of the Fermi level but they are also reproducible within one order of magnitude.

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