STUDY OF SOME STRUCTURAL PROPERTIES OF HYDROGENATED AMORPHOUS SILICON THIN FILMS PREPARED BY RADIOFREQUENCY CATHODIC SPUTTERING

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Abstract

In this work, we have used the grazing X-rays reflectometry technique to characterise hydrogenated amorphous silicon thin films deposited by radio-frequency cathodic sputtering. Reflectometry measurements are taken immediately after films deposition as well as after having naturally oxidised their surfaces during a more or less prolonged stay in the ambient. For the films examined just after deposition, the role of hydrogen appears in the increase of their density. For those analysed after a short stay in the ambient, hydrogen plays a protective role against the oxidation of their surfaces. This role disappears when the stay in the ambient is so long.
I- INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) is an interesting semiconductor material which has now wide technological applications such as solar cells for photovoltaic conversion, thin film transistors for liquid crystal flat panel displays, image sensors for document scanning, optical memory devices, medical X-ray imaging etc. [1-3]. Although the specific requirements of these various applications are different, their common need of a semiconductor material which is cheap, relatively simple in preparation and can be made in large areas has driven the development of the exceptional and particularly interesting physical properties of a-Si:H material. For example, from the photovoltaic conversion point of view, a-Si:H is distinguished by an optical gap in the required range for optimal performance [4]. It presents also a high optical absorption within the maximum of solar spectrum. So, a large part of solar energy is absorbed in a small thickness of the material allowing making structures in the form of very thin layers. Moreover, a-Si:H does not suffer light induced degradation (Staebler-Wronski effect) [5]. All these characteristics are of great importance making it a more attractive material for the elaboration of cheap photocells with good photovoltaic parameters. In addition, in microelectronic applications, its higher carrier mobility and higher doping efficiency could potentially allow the fabrication of an integrate circuit on glass using thin film transistor technology, making possible integrated driver circuits for flat panel displays. Therefore, for further development of new applications, it would be required to understand fundamental items, which the above applications are made on the basis of.

Physical properties that distinguish a-Si:H material depend closely on the manufacturing techniques involved, the experimental conditions of its preparation and, above all, the quantity of hydrogen it contains. In our previous work [6-8] we have prepared a-Si:H thin films by radio frequency cathodic sputtering technique and we have studied how optical characteristics of these films change with increasing hydrogen pressure during the deposition stage as well as with classical post-deposition annealing. We have shown that low hydrogen pressures allow a saturation of dangling bonds in the material, while high pressures lead to the creation of new defects. We have shown also that thermal annealing under moderate temperature allows a good improvement of the structural quality of deposited films [6-8].
In the present work, we use the grazing x-rays reflectometry technique to characterise some of the structural properties of a-Si:H very thin layers immediately after deposition as well as after surface oxidation or annealing.

II- EXPERIMENTAL DETAILS

II -1- Sample preparation

Starting from a silicon polycrystalline target under reactive ions of argon and hydrogen plasma, a-Si:H thin films of about 0.5 μm thick, and 1 cm² area are deposited by radio frequency cathodic sputtering technique [9]. The experimental set-up we have used is a full computerised system, model SCM 451, from Alcatel. It consists of a sputtering enclosure which allows depositions at different temperatures, a pumping system allowing reaching a vacuum of about 10⁻⁷ mbar, and a radio-frequency source with a 0 – 500 W power range. The substrates we have used are made of corning glass C7059. Before each deposition, both the sputtering enclosure and substrates are submitted to an appropriate cleaning to prevent the eventual contamination of silicon films.

Many a-Si:H thin films have been deposited by sputtering the polycrystalline silicon target under a constant pressure of 10⁻² mbar and 250W radio-frequency power. The temperature of the substrate and the distance target-substrate are respectively 25°C and 6 cm. The partial pressure of hydrogen introduced in the enclosure was ranged from 0 to 20% of the total pressure. Thin films obtained are stoechiometric with a good adherence. Some of them were characterised immediately after deposition without undergoing any particular processing. Others were examined after being oxidised in the ambient. In table I, we give some experimental details of deposited samples, such as hydrogen partial pressure and the post-deposition processing.

II -2- Experimental analyses

Deposited films have been examined by the grazing X-rays reflectivity technique [10]. This well-known technique is of great interest in surface science, since it allows the structure of the uppermost layers of a material to be probed. It consists in sending on the sample a monochromatic parallel beam of X-rays in the grazing incidence condition and recording the
evolution of the reflected beam intensity $I$ as a function of the variations of the incidence angle $\alpha$. The analysis of the experimental curves $I(\alpha)$ obtained allows the determination and/or the calculation of thickness, refractive index, roughness and both mass and electronic densities of very thin films while noise and other parasitic effects resulting from the films supports are minimised [10].

From the general optical basic concepts [10], it was shown that the refractive index $n$ of matter for X-ray radiation is:

$$n = 1 - \delta - i\beta$$  \hspace{1cm} (1)

The classical model of an elastically bound electron yields the following expression of $\delta$:

$$\delta = \frac{\lambda^2}{2\pi} r \rho$$  \hspace{1cm} (2)

where $r$ is the classical electron radius ($r = 2.81 \times 10^{-5}$ Å), $\lambda$ is the X-rays wavelength and $\rho$ is the electron density of the material. This shows that the real part of the refractive index $n$ mainly depends on the electron density of the material and on the wavelength $\lambda$. The imaginary part $\beta$ of $n$ is related to the linear absorption coefficient $\mu_L$ of the material by the following equation:

$$\beta = \frac{\lambda \mu_L}{4\pi}$$  \hspace{1cm} (3)

Typical values for $\delta$ are $10^{-5} - 10^{-6}$ and $\beta$ is ten times smaller.

A specific property of X-rays is that since the refractive index is slightly less than 1, a beam impinging on a flat surface can be totally reflected. The condition to observe total external reflection is that the angle of incidence $\alpha$ (defined as the angle between the incident ray and the surface) must be less than a critical angle $\alpha_c$. This angle can be obtained by applying the Snell-Descartes'law ($n \cos \alpha_c = \cos \alpha$) with $\cos \alpha_c = 1$, yielding in absence of absorption:

$$\cos \alpha_c = n = 1 - \delta$$  \hspace{1cm} (4)

Since $\delta$ is of the order of $10^{-5}$, the critical angle for total external reflection is clearly extremely small. At small angles, $\cos \alpha_c$ can be approximated as $1-\alpha_c^2/2$ and equation 4 becomes:

$$\alpha_c^2 = 2\delta$$  \hspace{1cm} (5)
The total external reflection of an X-ray beam is therefore only observed at grazing angles of incidence below about $\alpha < 0.5^\circ$. At larger angles, the reflectivity decreases very rapidly [10].

The absorption of the X-rays in the material depends on the complex part of the refractive index $n$ and limits the penetration of the beam inside the medium. The X-rays penetration depth $\tau$, defined as the distance for which the beam is attenuated by $1/e$, is given by [10]:

$$\tau(\alpha) = \frac{\lambda}{4\pi B(\alpha)}$$

where $B(\alpha)$ is the imaginary part of $(\alpha^2 - 2\delta - 2i\beta)^{1/2}$. Note that this quantity depends on the incident angle $\alpha$ through the value of $B(\alpha)$. In particular, in the limit $\alpha \to 0$, neglecting absorption:

$$\tau(\alpha_c) = \frac{\lambda}{4\pi \alpha_c}$$

In addition, the penetration depth $\tau$ is wavelength dependent since $\beta$ depends on the $\lambda$. Values of $\beta$ are tabulated [11] and they can also be found at the web site which has already been referred to [12].

It has been shown that $\tau$ remains small and below about 30Å when $\alpha$ is smaller than the critical angle $\alpha_c$. This is precisely the property which is exploited in surface diffraction, where only the first few atomic layers are analysed. After, $\tau$ increases steeply at the critical angle and finally slowly grows when $\alpha \gg \alpha_c$ [10].

To determine parameters such as thickness, mass and electronic densities, the method of calculation depends closely on the how many layers composing the considered film. In the literature, we found several calculations methods [13, 14]. Among them, we give below those we have used to characterise our mono-layer and bi-layer deposited thin films.

$\alpha$ values for the maximal and minimal interference fringes are related to the thin film thickness $l$ values by the modified Bragg's law [14]:

$$\sin^2 \alpha_{pi} = \alpha_c^2 + (p_i + \Delta p)^2 \frac{\lambda^2}{4l^2}$$
where $\alpha_{p_i}$ is the maximal or minimal angular position of the $i^{th}$ interference fringe of $p$ order. $\Delta p$ is equal to 1/2 for a maximum and zero for a minimum. The variation of $\sin^2 \alpha_{p_i}$ versus $(\pi_i + \Delta p)^2$ is linear whose slope $(\lambda / 2l)^2$ gives the thickness $l$ and the intercept determines the value of $\alpha_c$ and allows the calculation of the mass density $N_z$ as well as the electronic density $\rho$ of the thin film [13].

For a bi-layer thin film having the following typical structure: layer 1 / layer 2 / substrate, the corresponding experimental curve will show a beat phenomenon which makes difficult the determination of the fringes order. This phenomenon is due to the superposition of two waves with respective angular frequencies:

$$\omega_1 = \frac{2l_1}{\lambda} \quad \text{and} \quad \omega_2 = \frac{2l_\text{tot}}{\lambda}$$

where $l_1$ is the thickness of layer 1 and $l_\text{tot}$ is the whole thickness of the film.

The average angular frequency is given by:

$$\frac{\omega_1 + \omega_2}{2} \approx \frac{1}{\Delta \theta_i}$$

where $\Delta \theta_i$ is the difference between two successive maximums. The modulation angular frequency is:

$$\frac{\omega_2 - \omega_1}{2} = \frac{1}{\Delta \theta_{\text{mod}}}$$

So,

$$l_1 = \frac{\lambda}{2} \left( \frac{1}{\Delta \theta_i} - \frac{1}{\Delta \theta_{\text{mod}}} \right)$$

$$l_\text{tot} = \frac{\lambda}{2} \left( \frac{1}{\Delta \theta_i} + \frac{1}{\Delta \theta_{\text{mod}}} \right)$$

and the thickness of layer number 2 is:

$$l_\text{tot} - l_1 = \frac{\lambda}{\Delta \theta_{\text{mod}}} = l_2$$
III - RESULTS AND DISCUSSIONS

III -1. Measurements performed just after sample deposition

These measurements were made on the samples A, B, C. The corresponding curves obtained are shown in figure 1. The method of calculation, given in paragraph II-1, enabled us to obtain the lines of fitting for the three examined samples (figure 2). The exploitation of these lines was made using a program based on the least squares method. In table II, we have presented the obtained results. We are particularly interested in the results relating to the two principal parameters that are the thickness / and the mass density $\rho$ of the layers. It is noted that $\rho$ increases with the partial pressure of hydrogen $P_{H}$, whereas $l$ evolves in the opposite direction. The same results were obtained in the optical measurements, where the increase of mass density is explained by the increase of refraction index and the decrease of thickness is due to the decrease of deposition velocity [7]. The increase of $\rho$ reflects the positive role of hydrogen in the densification of the layers due to the saturation of dangling bonds.

III -2. Measurements performed after thermal annealing

Another sample (D), prepared under the same conditions as sample (C), was annealed before being measured by X-rays reflectivity (figure 3). Thermal annealing was done in a conventional furnace, at a temperature of 500°C, during 30 min. under a vacuum of $10^{-4}$ mbar. Figure 4 is the linear fitting of the experimental curve in figure 3. It shows a line whose exploitation gives experimental parameters presented in the last raw of table II. The comparison between these values with those obtained on the similar not annealed sample (sample C) shows a clear $\rho$ increase and $l$ decrease. These modifications due to the annealing treatment could be the result of an atomic rearrangement due to a partial re-crystallisation process in the deposited layer [15-17]. The increase of $\rho$ is represented by an increase in refraction index calculated from optical measurements using transmission spectra [6-8]. Indeed, the results of the literature show that, during a traditional thermal annealing, amorphous silicon crystallises at a critical temperature between 550°C and 700°C [15-17].
In figure 5, we have presented in logarithm scale the variation of X-rays penetration depth \( \tau \) in a function of the incidence angle \( \alpha \) for samples A and D. We observe that in the low \( \alpha \) \((\alpha < 0.22^\circ)\), \( \tau \) in sample A (without hydrogen) is slightly deeper than in the other sample. This is due to the fact that sample A mass density \( \rho \) is lower. For higher values of \( \alpha \), \( \tau \) increases first steeply at \( \alpha_c \) and slowly to reach a similar level for both A and D.

**III -3- Measurements performed after surface oxidation**

After the deposition and before taking reflectometry measurements, samples E, F and G are initially remained in the ambient for a long or short time without being directly exposed to solar radiations. \( I(\alpha) \) curves taken on each sample are shown in figure 6. Curves 6-a and 6-b present a beat phenomenon. This means that the corresponding samples E and F present an oxide coating on their surface. The oxide layer would be naturally formed during the long stay of these samples in the ambient.

From the analysis of the three experimental curves a, b and c (figure 6), we have deduced the values of the characteristic parameters shown in table III. For samples E and F that remained in the ambient for the same period (40 days), we found that the thickness \( l_{ox} \) and the electronic density \( \rho_{ox} \) of the oxide coating are larger in the sample E which was deposited without any hydrogen incorporation. This could be explained by the fact that hydrogen existing in sample F reduces the density of defects acting as nucleation centres for oxide growth [17]. Moreover, during the deposition when the partial pressure of hydrogen increases, the density of Si-Si bonds decreases while that of Si-H bonds, which are energetically more stable [18], increases. So, the more the sample is hydrogenated, the more its oxidation is slow.

Figure 6-c giving \( I(\alpha) \) for the sample G does not show Kiessing fringes. Since this sample was remained in the ambient for a very long time (six months), it should be oxidised so much that its thickness exceeded the typical value of 2000 \( \text{Å} \), which limits our calculation validity [19].

Finally, it will be interesting to notify that the density of oxide formed on the surface of our samples is lower than that of silice (SiO\(_2\)). This indicates that the formed oxide layer contains a high density of vacancies and thus it is quite fragile.
IV- CONCLUSION

In this work we have used the grazing X-rays reflectivity technique to characterise various a-Si:H thin films deposited by radio-frequency cathodic sputtering. Analysis of experimental curves obtained from examined samples enabled us to determine some physical parameters, particularly the thickness and mass density of deposited layers. We show that, when the partial pressure of hydrogen during the deposition process raise, the density of deposited layers increases and their thickness decreases. These results are explained by the fact that increasing the hydrogen concentration in the deposition reactive plasma leads to both layers densification mechanism, resulting from dangling bonds saturation, and a deposition rate reduction. We show also that hydrogen plays a protective role against surfaces oxidation of deposited layers staying in the ambient for a short time. This role disappears when the stay duration in the ambient is so long.

Owing to the fact that X-rays reflectivity technique works in the ambient, samples studied immediately after their deposition should normally present a very thin natural oxide layer on their free surfaces. However, the thickness of such oxide layer is so thinner that it has no negative effect on the calculation method we have used. In our progressing work, we are trying to determine experimentally the thickness of this layer.

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REFERENCES

[1] R. A. STREET, S. NELSON, L. ANTONUK and V. P. MENDEZ, 

JACKSON and P. NYLEN, 

Amorphous and Heterogeneous Silicon Thin Films: Fundamentals to Devices 

[4] J. LOFERSKI, 

PELLATON VAUCHER, Ch. HOF, D. FISCHER, H. KEPPNER, A. SHAH, K.-D. 
UFERT, P. GIANNFOLES and J. KOEHLER, 

[6] K. MELLASSI, M. CHAFIK EL IDRISSSI, A. CHOUIYAKH, A. RJEB and 
A. BARHDADI. 

[7] K. MELLASSI, M. CHAFIK EL IDRISSSI, A. CHOUIYAKH, A. RJEB and 
A. BARHDADI. 
will appear in the next issue of Revue des Sciences et Technologie.

[8] K. MELLASSI, M. CHAFIK EL IDRISSSI, A. CHOUIYAKH, A. RJEB and 
A. BARHDADI. 
will appear in the next issue of Physical and Chemical News.

[9] A. BENNOUNA, A. HAOUNI, N. GHERMANI and E-L. AMEZIANE, 

[10] J. DAILLANT and A. GIBAUD, 
X-Ray and Neutron Reflectivity: Principles and Applications 


[13] P. CROCE ET L. NEVOT, 
[14] L. V. AZAROFF,
Elements of X-ray Cristallography,

[15] Y. LAAZIZ, A. BENNOUNA and E. L. AMEZIANE,

[16] J. M. BERGER,
Thèse de doctorat d'Etat, Montpellier, 1985, France.

[17] A. BARHDADI et J-C. MULLER,
ICTP Preprint, IC / 98 / 130, Trieste 1998, Italy.

[18] R. W. COLLINS, C-Y. HUANG, AND H. WINDIXHMANN,

[19] KIESSING NATURWISSEN SCHAFTEN,
**Table I:** Experimental details of examined samples: hydrogen partial pressure during their deposition process and the kind of post-deposition processing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hydrogen partial pressure</th>
<th>Post-deposition processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>$10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>$2 \cdot 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>$2 \cdot 10^{-3}$</td>
<td>Annealing at 500°C during 30 mn</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>Oxydation in the ambient during 40 days</td>
</tr>
<tr>
<td>F</td>
<td>$5 \cdot 10^{-4}$</td>
<td>Oxydation in the ambient during 40 days</td>
</tr>
<tr>
<td>G</td>
<td>$2 \cdot 10^{-3}$</td>
<td>Oxydation in the ambient during six months</td>
</tr>
</tbody>
</table>
**Table II:** Parameters values determined from X-rays analyses performed on the samples A, B, C, and D.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hydrogen partial pressure $P_H$ (mbar)</th>
<th>Thickness $l$ (Å)</th>
<th>Critical angle $\alpha_c$ (degree)</th>
<th>Electronic density $N_Z$ (e. cm$^{-3}$)</th>
<th>Mass density $\rho$ (g. cm$^{-3}$)</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>958</td>
<td>0.2026</td>
<td>5.8649 $\times 10^{23}$</td>
<td>1.9554</td>
<td>6.2572 $\times 10^{-6}$</td>
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<tr>
<td>B</td>
<td>$10^{-3}$</td>
<td>522</td>
<td>0.2185</td>
<td>6.8193 $\times 10^{23}$</td>
<td>2.2736</td>
<td>7.2756 $\times 10^{-6}$</td>
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<tr>
<td>C</td>
<td>$2.10^{-3}$</td>
<td>470</td>
<td>0.2187</td>
<td>6.8327 $\times 10^{23}$</td>
<td>2.2781</td>
<td>7.2898 $\times 10^{-6}$</td>
</tr>
<tr>
<td>D</td>
<td>$2.10^{-3}$</td>
<td>445</td>
<td>0.2207</td>
<td>6.9557 $\times 10^{23}$</td>
<td>2.3191</td>
<td>7.4211 $\times 10^{-6}$</td>
</tr>
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</table>
Table III: Parameters values determined from X-rays analyses performed on the samples E, F and G.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hydrogen partial pressure $P_H$ (mbar)</th>
<th>$\Delta \theta$ (degree)</th>
<th>$\Delta \theta_{\text{mod}}$ (degree)</th>
<th>Total thickness $l_{\text{tot}}$ (Å)</th>
<th>Oxide layer thickness $l_{\text{ox}}$ (Å)</th>
<th>Silicon layer thickness $l_{\text{Si}}$ (Å)</th>
<th>Electronic density of thin oxide layer $10^{23}$ e. cm$^{-3}$</th>
<th>Mass density of thin oxide layer $\rho_{\text{ox}}$ (g . cm$^{-3}$)</th>
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<tr>
<td>E</td>
<td>0</td>
<td>0.04</td>
<td>0.29</td>
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<td>952</td>
<td>305</td>
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<td>F</td>
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<td>0.06</td>
<td>0.58</td>
<td>812</td>
<td>660</td>
<td>152</td>
<td>6.4063</td>
<td>2.1318</td>
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<tr>
<td>G</td>
<td>$2 \times 10^{-3}$</td>
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<td>-</td>
<td>&gt;2000 Å</td>
<td>-</td>
<td>-</td>
<td>6.5829</td>
<td>2.1906</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

**Figure 1:** Semi-logarithmic plotting of the reflected intensity $I$ according to the incidence angle $\alpha$ for three samples A, B and C examined immediately after deposition.

a) Sample A prepared without hydrogen incorporation ($P_H = 0$ mbar).
b) Sample B prepared with hydrogen partial pressure $P_H = 10^{-3}$ mbar.
c) Sample C prepared with hydrogen partial pressure $P_H = 2 \cdot 10^{-3}$ mbar.

**Figure 2:** Linear fitting of experimental curves shown in figure 1, performed by drawing $\sin^2(\alpha_p)$ versus $(p+1/2)^2$ where $p$ is the fringe order and $\alpha_p$ its angular position.

a) for the sample A,
b) for the sample B,
c) for the sample C.

**Figure 3:** Semi-logarithmic plotting of the reflected intensity $I$ versus the incidence angle $\alpha$ for the sample D analysed after thermal annealing.

**Figure 4:** Linear fitting of the experimental curve shown in figure 3.

**Figure 5:** Logarithmic variations of the penetration depth $\tau$ versus the incidence angle $\alpha$ for samples A and D.

**Figure 6:** Semi-logarithmic plotting of the reflected intensity $I$ versus the incidence angle $\alpha$ for the three samples E, F and G studied after surface oxidation.

a) for sample E,
b) for sample F,
c) for sample G.
Figure 2
Figure 3

Figure 4
Sample A ($P_H=0$ mbar)
Sample D ($P_H=2 \times 10^{-3}$ mbar)

Figure 5
Figure 6