

Optical characterization of a-Si:H thin films grown by Hg-Photo-CVD

A. Barhdadi^{1*}, S. Karbal¹, N. M'gafad¹, B. M. Aka²

¹*Laboratoire de Physique des Semi-conducteurs et de l'Energie Solaire (P.S.E.S.)*

Ecole Normale Supérieure, P.O. Box: 5118, Takaddoum, Rabat 10000, Morocco

Unité de Formation et de Recherche en Physique de la Matière Condensée et Modélisation Statistique des Systèmes,

Faculty of Sciences, University Mohammed V-Agdal, Rabat 10000, Morocco

²*Département des Sciences et Technologie, Ecole Normale Supérieure, University Abobo-Adjamé*

P.O. Box 1561, Abidjan 22, Côte d'Ivoire

**The Abdus Salam International Centre for Theoretical Physics (ICTP), 34014, Trieste, Italy*

Mercury-Sensitized Photo-Assisted Chemical Vapor Deposition (Hg-Photo-CVD) technique opens new possibilities for reducing thin film growth temperature and producing novel semiconductor materials suitable for the future generation of high efficiency thin film solar cells onto low cost flexible plastic substrates. This paper provides some experimental data resulting from the optical characterization of hydrogenated amorphous silicon thin films grown by this deposition technique. Experiments have been performed on samples deposited at different temperatures, with and without thermal annealing.

Keywords : Photovoltaic, Solar Cell, Thin films, Nano-Crystalline Silicon, Hydrogenated Amorphous Silicon, Optical Properties, Thermal Annealing

PACS : 68.60.Dv , 78.66.Jg , 78.66.-w , 73.50.Pz , 81.15.-z , 84.60.Jt

I. INTRODUCTION

Hydrogenated amorphous Silicon (a-Si:H) is one of the most attractive semiconductor materials for the elaboration of thin, flexible and cheap solar cell devices [1 - 4]. It is distinguished by a large optical gap in the required range for optimal PV conversion, and a high optical absorption within the maximum of solar spectrum [9]. So, a large part of solar energy is absorbed in a small thickness of the material allowing to make solar cells in the form of very thin films.¹

The performances of a-Si:H solar cells are intimately related to the film structure determined by the preparation method and the experimental conditions adopted during the deposition process. Various deposition techniques have been employed [13 - 18]. Among them, Plasma-Enhanced Chemical Vapor Deposition (PECVD) [18 - 23] still the most commonly used for the direct growth of a-Si:H thin films on low substrate temperature, and SiH₄ heavily diluted with H₂, are generally used as the reactants. However, PECVD has yet two serious drawbacks: the surface damages which result from the impinging charged particles with

high energy of the plasma, and the impurities incorporation which results from sputtering because of the high potential difference between substrate and electrodes in the reactor [24]. Recently, Myong et al. [30] reported that Mercury-Sensitized Photo-Assisted Chemical Vapor Deposition (Hg-Photo-CVD) is an efficient method for depositing high quality a-Si:H thin films at temperature as low as 120°C. They also showed how this technique is promising for developing an innovative generation of nano-crystalline silicon (nc-Si) thin film solar cells fabricated onto low cost flexible plastic substrates.

At home laboratory, after a long time working on a-Si:H thin films prepared by radio frequency cathodic sputtering technique [25 - 29], we are presently focusing on Myong et al. achievements and trying to perform some significant original contributions in this new topic. So, the conception and realization of a new a-Si:H thin films deposition set up based on the Mercury-sensitized photo-CVD technique [31 - 33] is progressively developed in our laboratory. This set up is quite similar to that performed by Aka some years ago in France [34 - 37]. The specific research program we are currently carrying out on this new system consists in depositing good quality a-Si:H and nc-Si thin films in the perspective to contribute in the development of the future generation of low cost powerful terrestrial solar cells. To conduct well this research program, we initially performed an extensive bibliographical work on

^{1*} Corresponding author (Senior Associate of the Abdus Salam ICTP) Phone: (212) 37 75 12 29 or (212) 37 75 22 61 or (212) 64 93 68 15 Fax: (212) 37 75 00 47
E-mails: barhdadi@ictp.it or abdelbar@fsr.ac.ma

fundamental points characterizing both a-Si:H and nc-Si materials and Hg-Photo-CVD technique. That is what we have tried to recall and review through the bibliographical synthesis we have published in recent papers [38 - 41].

In the present work, we provide the readers with some experimental results we have obtained on this subject. We have prepared a-Si:H thin films using the Hg-Photo-CVD technique and we have studied how optical characteristics of these films change with increasing the substrate temperature during the deposition and what effects may be observed from a post-deposition thermal annealing.

II- EXPERIMENTAL DETAILS

II-1- Description of Hg-Photo-CVD system

The Hg-photo-CVD set up we developed in our laboratory is very simple. Its schematic diagram (figure 1) is described elsewhere [38 - 41]. It consists mainly of a cylindrical horizontal quartz reactor in the form of a special tube with size and dimensions as specified in figure 2. This tube, used as a deposition chamber, has two access gates for the entries and exits of gases. It is equipped with a small reservoir containing a small quantity of liquid mercury (Hg bath) which can be thermally controlled independently of the remainder of the system. The inner surface of the tube may be coated with low-vapor-pressure Fomblin vacuum oil to prevent any film deposition on [42 - 44]. The substrate support has a rectangular form and can be of graphite or of stainless steel. It is heated through a thermo-coax wire and equipped with a Chromel-Alumel thermocouple to measure the substrate temperature T_s in a wide range [200°C, + 1000°C]. Well-cleaned high resistivity crystalline Si wafers or Corning 7059 glass can be used as substrates. The distance between the tube inner surface and substrates is about 3 cm. The UV light source consists of a series of PHILIPS-TUV low pressure Hg lamps radiating both 253.7 nm (40 mW/cm² or ~ 30 mW/cm² at 3 cm distance) and 184.9 nm (less than 10 mW/cm² or ~ 5 mW/cm² at 3 cm distance) resonance lines. Since the transmittance of the quartz tube for the 253.7 nm and 184.9 nm wavelengths is 82 % and 20 % respectively, the 253.7 nm resonance line of UV light is dominantly irradiated into the reactor. The series of Hg lamps are set up under an aluminum reflector placed at about 5 cm distance from the reactor. The vacuum system is composed of two pumps. The first one, with pallets, is used to obtain a primary vacuum and to purge gases of the reactor. The second is a diffusion pump allowing evacuation down to a pressure of 10⁻⁶ Torr during the back out of the reactor prior to the growth. The inside total gas pressure is adjusted by a conductance valve and measured by a MKS Baratron capacitance manometer placed rightly in the entry of the reactor. This manometer has the advantage to indicate pressure values independently to

the nature of gas used, contrary to the Pirani gauges that we have associated to the vacuum pumps. Reactant gases, mainly SiH₄ and H₂, are introduced into the reactor through the Hg bath usually kept at a temperature between 35°C and 50°C. Thus, a very small amount of Hg vapor is automatically mixed with the gases and introduced into the deposition chamber. The Hg vapor atoms, then introduced, enhance the dissociation of SiH₄ [45] because of its weak optical absorption in the 190-200 nm wavelengths region [46, 47].

Because our Hg-photo-CVD set up is quite similar to that performed by Aka [34 - 37], we suppose that experiments we may conduct on both systems in the same conditions should provide the same results.

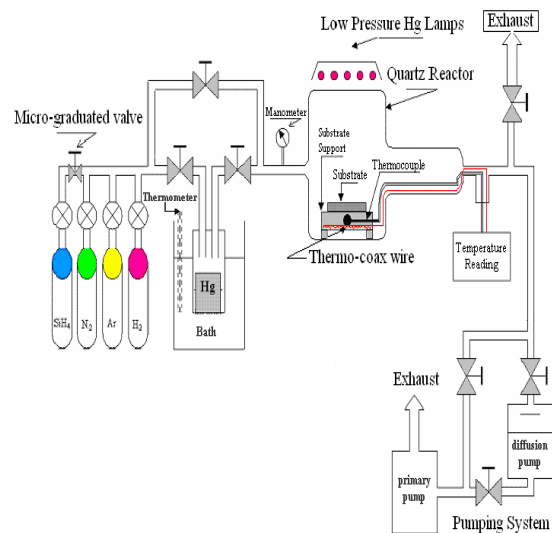
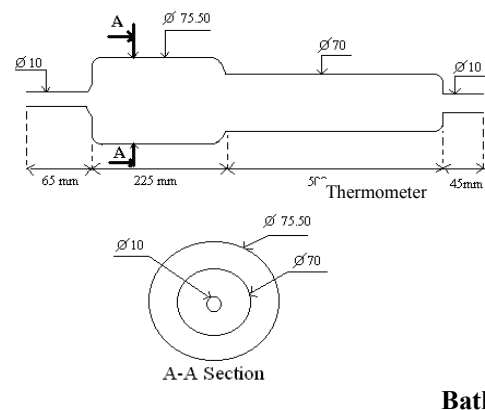


Figure 1: Schematic diagram of the Hg-sensitised Photo-CVD set up developed at home laboratory



Bath

Figure 2: Schema and size dimensions of the cylindrical horizontal quartz reactor used

II-2- Sample preparation

The a-Si:H thin film samples were deposited from the photodissociation of SiH₄ reactant gas mixed

with N₂ buffer inert gas. This dilution is required for both economical and safety reasons since the presence of N₂ at high enough concentration eliminate the explosive character of some hazardous reactions as specified in the literature [48]. The gas mixture was introduced into the reactor through the Hg bath to carry a very small amount of mercury vapor. The SiH₄ flow is controlled by a micro-valve. The substrates used are of Corning 7059 glass with a small surface of about 1 cm². Before any deposition, they have been submitted to an appropriate cleaning to prevent eventual

Substrate : Corning glass C 7059
Base pressure : 10 ⁻⁶ Torr
Total deposition pressure (P) : 5 Torr
Growth temperature (T _s) : Ranging from 100°C to 400°C with 100°C step
Silane flow rate : 1 sccm
Total lamp power : 2 mW/cm ²
Hg bath temperature: 50°C

Table 1: Summary of growth conditions

III-3- Experimental analyses

The whole hydrogen concentration as well as its spatial distribution in the films was determined by the ERDA technique [49]. Their optical properties were measured by means of a Beckman UV-5270 spectrophotometer operating with a double beam in a wide spectral range (0.25 μm - 3 μm). Transmission measurements were taken by means of the differential method [50] which consists in determining the transmission of the layer together with its substrate by comparison to another identical virgin substrate used as reference. Under these conditions, the influence of the substrate on the transmitted light is practically negligible [50]. Some samples have also been characterized using Infra-Red Spectroscopy measurements to look at how hydrogen atoms are bonding within the lattice.

III - RESULTS AND DISCUSSIONS

Thin films obtained were characterised immediately after deposition without undergoing any particular processing. Some of them were examined before and after being thermally annealed.

III -1- Measurements performed just after thin films growth

These measurements were performed on a-Si:H thin films deposited on substrates whose temperature ranges from T_s = 100°C to T_s = 400°C by 100°C step. In order to determine the total concentration of hydrogen in these as-deposited films, ERDA measurements have been

contaminations. Indeed, they were degreased in trichlorethylene, cleaned in acetone, carefully rinsed in running de-ionised water, and finally dried under a nitrogen gas flow, before placing them into the reactor. The substrate temperature (T_s) being the main parameter that we intended to vary, substrates were then inserted in the reactor and heated up the desired temperature ranged from 100°C to 400°C by step of 100°C. Table 1 summarizes all our experimental growth conditions. They have been chosen on the basis of results deduced from previous works [34]. After 30 min deposition run, thin films obtained are with a good adherence. They are supposedly homogeneous and their thickness is uniform and does not exceed 0.5 μm.

systematically performed on all of them. The results are summarized in table 2. We can easily note that thin films are, in general, highly hydrogenated. This could be explained by the SiH₄ low flow we have used for the films growth process [34]. We can also clearly note that hydrogen relative content in the films decreases quite regularly according to increase of their growth temperature.

T _s (°C)	[H] / [Si] (%)
100	42
200	30
300	20
400	13

Table 2: Hydrogen relative concentration in the films according to the growth temperature T_s

Figure 3 shows a typical transmission spectrum (normalized to that of the substrate) obtained for the a-Si:H thin film deposited at T_s = 200°C. All the other transmission spectra obtained for the different a-Si:H samples deposited at various T_s practically present the same form. They all exhibit two clearly distinct slopes [51]. The first one, in which interference fringes (oscillations) are seen, is commonly named the transparency zone or the zone of weak absorption. In the second one, which is well known as the zone of high absorption, the signal is strongly reduced.

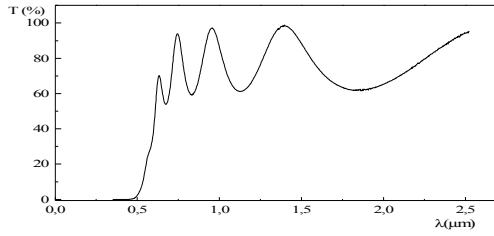


Figure 3: Transmission spectra, normalised to the substrate, for a-Si:H thin film deposited at 200°C.

By exploiting the different transmission spectra corresponding to the various T_s values, and using the mathematics expressions reported in reference [52], we were able to determine the main optical characteristics of our samples, especially the refraction index (n), the optical gap (E_g) and the Urbach energy (E_u) [53]. It should be interesting to remember that the latter draws light on the density of the energy states localised in the tail of the valence band, which are generally attributed to the structural disorder in the material [54].

In figure 4, we reproduce the dependence of refraction index n with the wavelength λ for all T_s considered. The values of n were adjusted using the dispersion law of Sellmeiere (equation 1) [55].

$$n^2(\lambda) = n_\infty^2 + \frac{b^2}{\lambda^2 - \lambda_0^2} \quad (1)$$

where n_∞ is the refraction index obtained by extrapolation towards the infinite; b and λ_0 are constants determined by the $n(\lambda)$ curve fitting.

From figure 4, we can note that n values are relatively low but similar to those obtained by both Zarnani et al. [56] and Toyoshima et al. [57] in the case of thin films photo-deposited from Si_2H_6 and Si_3H_8 by means of Excimer laser emitting at 193 nm. It is also clear that, when T_s increases, $n(\lambda)$ curve shifts towards higher n values. This evolution, which has already been observed by many other authors [56, 58 - 60], should be closely associated to the hydrogen concentration in the layers. In others words, when the hydrogen content decreases, the density of dangling bonds in the film increases in parallel with the layer absorption and, then, an enhancement of the refraction index is observed. Indeed, for a given material, the more its absorption is higher, the more light reflection at its surface is better (metallic luster).

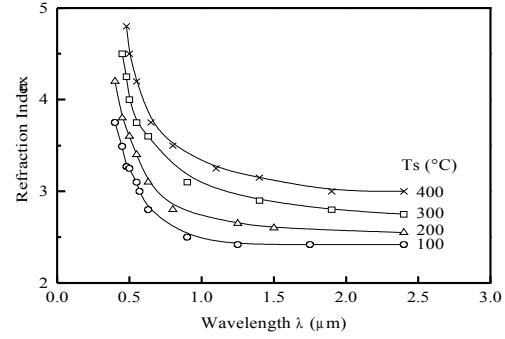


Figure 4: Evolution of the refraction index n with the wavelength λ for various T_s .

Figure 5 shows the evolution of E_g and that of E_u as functions of T_s . E_g values were determined from the Tauc formula [61] expressed by equation 2, and those of E_u from the Urbach law [53] formulated by equation 3.

$$(\alpha \, h\nu)^{1/2} = B (h\nu - E_g) \quad (2)$$

$$\alpha(h\nu) = \alpha_0(h\nu) \exp\left(\frac{h\nu - h\nu_0}{E_u}\right) \quad (3)$$

α is the absorption coefficient, $h\nu$ is the photon energy, B is a coefficient of proportionality, α_0 and $h\nu_0$ are constants depending on depositing conditions of the films.

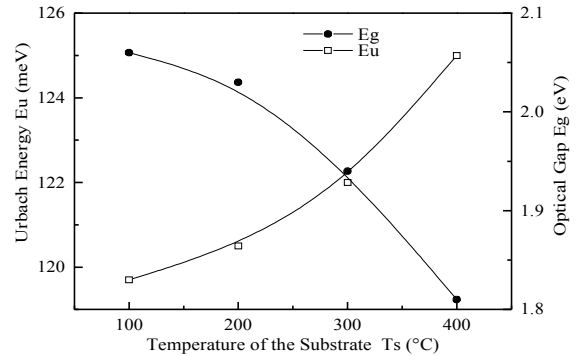


Figure 5: Evolution of the optical gap (E_g) and of the Urbach energy (E_u) measured on deposited layers as functions of substrate temperature T_s .

We notice that E_g and E_u evolve into strictly opposing directions: when one increases the other decreases. This clearly confirms the very close relationship existing between these two parameters because of the presence of a more or less important density of dangling bonds in the material.

Figure 5 also shows that, when T_s increases, E_g decreases quickly. Co-jointly, E_u perfectly develops in the opposite direction. From these results, we can say that for low T_s , hydrogen incorporation saturates dangling bonds in the deposited layers. This leads to a clear improvement of E_g and E_u . When $T_s = 100^\circ\text{C}$, the density of dangling bonds is minimal and hence, the optical performances of the layers are optimal (E_g is maximal and E_u is minimal). When T_s becomes high and higher, the out diffusion of hydrogen from the material should be more and more important. The less presence of hydrogen in the material generates new structural defects. This has negative repercussions on the optical performances of the layers, and leads to a diminution of E_g , accompanied by an increase of E_u , as seen in figure 5.

III -2- Measurements performed after thermal annealing

After examining the effects of growth temperature on the optical properties of a-Si:H thin films immediately after their photo-depositing, we focused on the changes that would affect these properties after thermal annealing. It is essential to keep in mind that stability of photovoltaic a-Si:H compounds depends on their normal functioning temperature and on the thermal solicitations to which they are sometimes compelled to be submitted. This is why many studies hold on this extremely important aspect of the problem [62 - 66].

The effect of annealing temperature T_a we are studying in this section is especially interesting for removing defects, inherently existing in the amorphous structure, in order to improve the conduction properties of the material.

While heating an a-Si:H sample, at least two main different situations may be observed. In the first one, a reversible annealing effect happens. This means the material optical parameters, such as α and n , recover their initial values at ambient temperature as soon as the heating is stopped. In this case, the material doesn't keep any trace of the annealing effect. In principle, this reversible effect should occur for annealing temperatures lower or closer to the growth temperature T_s . In the second possible situation, an irreversible annealing effect happens. This means that heating has modified the material properties and, therefore, measurements at the ambient temperature couldn't give back the initial values of parameters.

To perform this part of work, we have prepared four a-Si:H samples under experimental conditions similar to those mentioned above, using a T_s fixed at 200°C . One of the samples is kept as a control. The other three were each submitted to 2 hours isochronal thermal annealing in a conventional furnace under 10^{-6} mbar vacuum. Annealing temperature T_a was chosen to

be the variable parameter of which we try to determine the effect. T_a was fixed at 340°C for the first annealing, at 400°C for the second and at 570°C for the third one. Since T_s was fixed at 200°C , the control has been considered therefore as a sample thermally annealed at $T_a = 200^\circ\text{C}$.

Figure 6 shows the spectral scattering of the refraction index n for all the annealed samples. We notice that thermal annealing induces a clear n increasing in the whole-explored spectral range. This increase is obviously slight for $T_a = 340^\circ\text{C}$ but, when T_a reaches 570°C , it becomes so important that, for high λ , n reaches typical values usually measured on silicon crystals [67]. With regard to this result, we can already say that thermal annealing at 570°C allows a partial crystallisation of the deposited layer. Hence, we meet literature data which show that amorphous silicon crystallises at a critical temperature between 550°C and 700°C during annealing process [64].

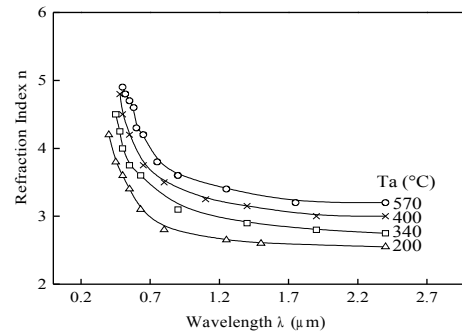


Figure 6: Evolution of the refraction index n with the annealing temperature T_a

In this context, it is most important to recall what Chahed et al. [63] have previously published on the basis of their experimental results obtained from X-rays analysis. They found that, for as-deposited a-Si:H thin films as well as for low temperature annealed ones, the film density is distinctly weaker than that of crystalline silicon. Only thermal annealing at temperature as higher as 600°C enhances the densification of the films and reduces significantly their thickness. Therefore, the evolution of the thin films optical parameters with thermal annealing should be examined according to the structural modifications of the layers. Basically, these modifications result from some hydrogen out-diffusion during thermal processing allowing the resurgence of structural defects depending strongly on how stable the various hydrogen configurations in the layers are. Indeed, thermal annealing at increasing temperature up to the crystallization stage produces a progressive out-diffusion of hydrogen. However, for the bounded hydrogen atoms, this out diffusion is generally observed for T_a distinctly higher than T_s . For the lower T_a , thermal processing only induces some homogeneity in the structure of as-deposited layers without any significant

effect on their electronic properties [63]. In contrast, thermal processing at much higher temperatures may induce thermal constraints generating new structural defects in the layers [66, 68, 69].

In figure 7, the variations of E_g and those of E_u with the annealing temperature T_a are both reported on the same graph. The first remark is the close relationship that links these two parameters making their evolution curves quite symmetric. Furthermore, these curves present an important similarity with those found in the literature [34].

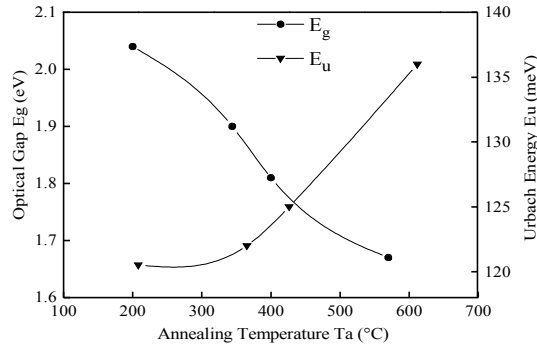


Figure 7: Variations of the optical gap E_g and the Urbach energy E_u according to the annealing temperature T_a .

The examination of the two curves above allows noting the following points:

a) For the non annealed sample (control), E_g and E_u present values practically equal to those measured above in the sample that was prepared in the same experimental conditions (figure 5). This proves that our results are reproducible. In other words, the structural quality of the deposited layers is practically influenced only by deposition experimental conditions which are entirely under control.

b) The irreversible effect starts at 200°C which is precisely the value of growth temperature T_s ($T_a = T_s$). Between 200°C and 570°C, E_g decreases from 2.04 eV to 1.67 eV.

c) Thermal annealing at 340°C or at 400°C simultaneously leads to a decrease in E_g and to a proportional increase in E_u . On the basis of literature data [34], we attribute this to a partial out-diffusion of hydrogen resulting from a break of the less stable bonds of SiH_2 and SiH_3 that have been formed in the material during the growth.

d) After annealing at 570°C, E_g decreases considerably reaching a value of 1.67 eV. Simultaneously, E_u increases to reach an average value of 136 meV. Logically, and in the same way as in the two first annealings operated at 340°C and 400°C, these variations can also be attributed to the out diffusion of a

higher quantity of hydrogen as a result of the break in the more stable bonds of Si-H [34, 70]. Nevertheless, this interpretation is not sufficient to explain well the changes we observed, even if we assume that the quantity of hydrogen incorporated in the material during depositing has wholly out diffused. Indeed, after an annealing at 570°C, E_g and E_u values are very different from those measured on a non annealed sample deposited in the same experimental conditions at a temperature $T_s = 570^\circ\text{C}$. This proves that, even if the out diffusion of hydrogen is total, it cannot explain by itself the observed results. Taking in consideration the values of E_g and E_u obtained, we think that the most plausible interpretation of our results should combine the hydrogen out diffusion phenomenon to an efficient process of crystallisation of the layers, which is well favoured by the high values of T_a [62, 65, 71, 72]. However, the creation of new structural defects in the material because of thermal constraints and heating is not excluded [73].

IV- CONCLUSION

The present paper is exclusively dedicated to the presentation of the new Hg-Photo-CVD set up we have developed at our laboratory, and the exposition of some experimental results obtained by these kinds of thin films photo-deposition systems. We have studied the effect of the substrate temperature T_s during the growth process, as well as the post-growth thermal annealing temperature T_a , on the optical parameters of a-Si:H thin films photo-deposited by this technique. Usually, in the photo-assisted process, the depositing rate increases with the intensity of UV light generated by the source of photons. In our study, because we have used the available low pressure Hg lamps as UV source, the thin films growth rate was relatively low. The obtained results show that as deposited thin films hold a very high quantity of hydrogen (about 40 % for $T_s = 100^\circ\text{C}$) and a small refractive index n in the visible range of light. The absorption thresholds as represented by the optical gap E_g are in the range of 1,58 eV and 2,2 eV. These results are close to those already published in the literature. For low T_s , hydrogen atoms saturate most of dangling bonds existing in the deposited layers. This is shown through the correct values obtained for the optical gap E_g and the Urbach energy E_u . For higher T_s , hydrogen begins to out-diffuse and the optical performances of the layers start decreasing.

After thermal annealings, at least two processes can be identified from the variation of optical parameters with annealing temperature T_a . The first one occurs when T_a is close to T_s or moderately higher such as 340°C or 400°C. It consists in the liberation and out-diffusion of a high quantity of hydrogen atoms, which are incorporated in the layers but weakly bounded in the matrix. Of course, this hydrogen out-diffusion should be

followed by a reconstruction of the material leading for some structural disorder. The second process is the matrix annealing which occurs when the annealing temperature is much higher than T_s . It is generally accompanied by the generation of a high density of dangling bonds in the material because of the broken strong Si-H bonds, the out-diffusion of extra hydrogen atoms and also the generation of new structural defects because of thermal constraints. However, at least a partial re-crystallisation of the layers should happen.

ACKNOWLEDGMENTS

This paper has been prepared on the basis of experimental results obtained essentially by the co-author B. M. Aka. It has been structured, enriched by literature data and written during the scientific stay of the first author A. Barhdadi, as Senior Associate Professor, at the Abdus Salam International Centre for Theoretical Physics (ICTP). This author would like to thank the Director and staff of the Centre for their kind hospitality, efficient assistance and great support. He also wishes to thank a lot Professor G. Furlan, Head of ICTP-TRIL Programme, for his precious scientific cooperation and paper expertise. Special thanks are also addressed to Profs. D. Sayeh and M. Abd-Lefdil, respectively the former and the present Directors of "Physique des Matériaux" Laboratory, Faculty of Sciences, University Mohammed V-Agdal, Rabat, for their great scientific and technical contributions.

REFERENCES

- [1] M. A. Green Third Generation Photovoltaics: Advanced Solar Energy Conversion Springer Series in Photonics, N°5, 2003
- [2] A. Goetzberger and V. U. Hoffmann Photovoltaic Solar Energy Generation Springer Series in Optical Sciences. N°112, 2005
- [3] W. Fuhs and R. Klenk, Thin film solar cells - Overview. Proceedings of the 2nd World Conference on Photovoltaic Solar Energy Conversion, Vienna, Austria, 1998, p. 381-386.
- [4] W. H. Bloss, F. Pfisterer, M. Schubert and T. Walter Progress in Photovoltaics, 3, 1995, pp. 3-24.
- [5] K. Zweibel International Journal of Solar Energy, 12, 1992, p. 285.
- [6] J. R. Tuttle, M. A. Contreras, A. M. Gabor, K. R. Ramanathan, A. L. Tennant, D. S. Albin, J. Keane and R. Noufi Progress in Photovoltaics, 3, 1995, p. 383.
- [7] D. Bonnet and M. Harr Proceedings of the 2nd World Conference on Photovoltaic Solar Energy Conversion, Vienna, Austria, 1998, p. 397-402.
- [8] M. Kondo and A. Matsuda Thin Film Solar Cells: Next Generation Photovoltaics and Applications Editor: Y. Hamakawa, 2004, Springer Series in Photonics
- [9] J. Loferski J. Appl. Phys., 27, 1956, p. 777.
- [10] D. E. Carlson, R. R. Arya, M. Bennett, L. F. Chen, K. Jansen, Y. M. Li, J. Newton, K. Rajan, R. Romero, D. Talenti, E. Twesme, F. Willing and L. Yang Proc. of the 25th IEEE Photovoltaic Specialists Conference (IEEE, Piscataway 1996), p. 1023.
- [11] S. Guha Proc. of the 25th IEEE Photovoltaic Specialists Conference (IEEE, Piscataway 1996), p. 1017.
- [12] S. Fujikake, K. Tabuchi, A. Takano, T. Wada, S. Saito, H. Sato, T. Yoshida, Y. Ichikawa and H. Sakai Proc. of the 25th IEEE Photovoltaic Specialists Conference (IEEE, Piscataway 1996), p. 1045.
- [13] Y. L. Wang, G. S. Fu, Y. C. Peng, Y. Zhou, L. Z. Chu and R. M. Zhang Chin. Phys. Lett., 21 (1), 2004, pp. 201-202
- [14] G. S. Fu, W. Yu, S. Q. Li, H. H. Hou, Y. C. Peng and L. Han Chin. Phys., 12 (1), 2003, pp. 75-78
- [15] W. Yu, B. Z. Wang, W. B. Lu, Y. B. Yang, L. Han and G. S. Fu Chin. Phys. Lett., 21 (7), 2004, pp. 1320-1322
- [16] M. Morales, Y. Leconte, R. Rizk and D. Chateigner J. Appl. Phys., 97 (3), 2005, pp. 4307-4320
- [17] H. R. Moutinho, C. S. Jiang, Y. Xu, B. To, K. M. Jones, C. W. Teplin, M. M. Al-Jassim Proc. of the 31st IEEE Photovoltaics Specialists Conference and Exhibition Lake Buena Vista, Florida, January 3-7, 2005
- [18] P. Roca i Cabarrocas Phys. Stat. Sol. C, 1 (5), 2004, pp. 1115-1130
- [19] J. Müller, F. Finger, R. Carrius and H. Wagner Phys. Rev. B, 60, 1999, p. 11666.
- [20] U. Kroll, J. Meier, A. Shah, S. Mikhailov and J. Weber J. appl. Phys., 80, 1996, p. 4971.
- [21] M. Kondo, Y. Nasumo, H. Mase, T. Wada and A. Matsuda J. Non-Crys. Solids, 299-302, 2002, p. 108.
- [22] S. Hamma, P. Roca i Cabarrocas J. Non-Crys. Solids, 227-230, 1998, p. 852.
- [23] P. Hapke and F. Finger J. Non-Crys. Solids, 227-230, 1998, p. 861.
- [24] K. Endo et al. Solar Energy Materials & Solar Cells, 66, 2001, p. 283.
- [25] K. Mellassi, M. Chafik El Idrissi, A. Barhdadi, A. Chouiyakh and A. Rjeb ICTP preprint, IC 2000, 128
- [26] K. Mellassi, M. Chafik El Idrissi, A. Barhdadi, A. Chouiyakh and A. Rjeb Sciences & Technologie, N°15, 2001, pp. 41-46.
- [27] K. Mellassi, M. Chafik El Idrissi, A. Chouiyakh, A. Rjeb and A. Barhdadi Physical and Chemical News, Vol. 6, 2002, pp 43-49
- [28] K. Mellassi, M. Chafik El Idrissi and A. Barhdadi ICTP preprint, IC 2001, 103
- [29] A. Barhdadi and M. Chafik El Idrissi ICTP preprint, IC 2002, 100 <http://arxiv.org/abs/cond-mat/0208601>
- [30] S. Y. Myong, T. H. Kim, K. S. Lim, K. H. Kim, B. T. Ahn, S. Miyajima and M. Konagai Solar Energy Materials & Solar Cells, 81, 2004, pp. 485-493.

- [31] Y. K. Su, C. J. Wang and Y. C. Chou Jpn. J. Appl. Phys., 28, 1989, p. 1644.
- [32] C. J. Hwang and Y. K. Su J. Electron. Mater., 19, 1990, p. 753.
- [33] C. J. Hwang and Y. K. Su J. Appl. Phys., 67, 1990, p. 3350.
- [34] B. Aka, Doctorate thesis, Louis Pasteur University, Strasbourg I, 1989, France.
- [35] B. Aka, J. Soc. Ouest Afr. Chim., 10, 2001, p. 119.
- [36] B. Aka, G.A. Monnehan, C. Fuchs and E. Fogarassy Rev. Iv. Sci. Tech., 2, 2001, p. 49
- [37] B. Aka and A. Trokourey, J. Soc. Ouest Afr. Chim., 9, 2000, p. 27
- [38] A. Barhdadi ICTP preprint, IC 2003, 102
- [39] A. Barhdadi Afrique Science, Vol 1, N°1, 2005, pp. 15-30
- [40] A. Barhdadi ICTP Preprint IC 2005, 069
- [41] A. Barhdadi Science Echoes Magazine, 4, 2006, pp. 27-53.
- [42] M. Konagai, T. Tanaka, K. W. Yeol and K. Takahashi E-MRS Proceedings, Strasbourg (1984) p. 551, Les éditions de Physique, Paris.
- [43] A. E. Delahoy, Solars Cells, 21, 1987, p. 153.
- [44] A.E. Delahoy, J. Non-Cryst. Solids, 77-78, 1985, p. 833.
- [45] T. L. Pollock, H. S. Sandhu, A. Jodhan and O. P. Strausz J. Am. Chem. Soc., 95, 1973, p. 1017.
- [46] H. J. Emeleus and K. Stewart Trans. Faraday Soc., 22, 1936, p. 1577.
- [47] J. H. Clark and R. G. Anderson Appl. Phys. Lett., 32, 1978, p. 46.
- [48] B. Aka and E. Boch Jour. of photochemistry and photobiology A: Chemistry, 150, 2002, p. 261.
- [49] J. P. Stoquert, M. Hage-Ali, J. L. Regolini, C. Ganter and P. Siffert E-MRS Proceedings, Strasbourg (1986) p. 159, Les éditions de physique, Paris.
- [50] G. D. Cody, C. R. Wronski, B. Abeles, R. B. Stephens, B. Brooks Solar Cells, 2, 1980, p. 227.
- [51] S. Guha 2nd Workshop on Science and Technology of Thin Films, 1996, Trieste, Italy
- [52] A. Bennouna, Y. Laaziz, M. A. Idrissi Thin Solid Films, 213, 1992, p. 55.
- [53] F. Urbach Phys. Rev. B, 92, 1953, p. 1324.
- [54] D. Jousse Doctorate Thesis, Université Scientifique et Médicale, Grenoble, 1983, France.
- [55] T. C. Anthony, A. L. Fahrembruch, R. H. Bube J. Cryst. Growth, 59, 1982, p. 289.
- [56] H. Zarnani, H. Demiryont and G. J. Collins J. Appl. Phys., 60, 1986, p. 2523.
- [57] Y. Toyoshima, K. Kumata, U. Itoh and A. Matsuda Appl. Phys. Lett., 51, 1987, p. 1925.
- [58] F. Demichelis, E. Minetti-Mezzetti, A. Tagliafero, E. Tresso, P. Rava and N. M. Ravindra J. Appl. Phys., 59, 1986, p. 611.
- [59] J. M. Berger, B. Yous, J. P. Ferraton and A. Donnadiou J. de Physique, Colloque C9, Suppl. au N° 12, Tome 43 (1982) C9-339.
- [60] R. J. Zanzucchi, C. R. Wronski and D. E. Carlson J. Appl. Phys., 48, 1977, p. 5227.
- [61] J. Tauc, R. Grigorovici and A. Vancu Phys. Stat. Solidi., 15, 1966, p. 627.
- [62] K. Zellama, J. H. Bardeleben, V. Quillet, V. Bouizem, P. Sladek, M. Theye, P. R. I Cabarrocas J. Non-Cryst. Solids, 285, 1993, p. 164-166.
- [63] L. Chahed, M. L. Theye, B. Bourdon J. Physique, 44, 1983, p. 387.
- [64] J. M. Berger Doctorate thesis, Montpellier, 1985, France.
- [65] G. D. Cody, T. Tiedje, B. Abeles, B. Brooks and Y. Goldstein Phys. Rev. Lett., 47(20), 1981, p. 1480.
- [66] G. D. Cody Semiconductors and Semimetals, Vol. 21, Part B: Optical Properties, Ed. J. I. Pankove, Academic Press, pp. 50-60.
- [67] E. D. Palik Handbook of Optical Constant of Solids, Academic Press Inc., Orlando, 1985, USA.
- [68] S. Yamasaki, N. Hata, T. Yoshida, H. Oheda, A. Matsuda, H. Okushi and K. Tanaka J. Physique, Colloque d'Orsay, France, 42, 1981, C4, p. 297.
- [69] M. Yoshida and K. Morigaki J. Non-Cryst. Solids, 59-60, 1983, p. 357.
- [70] K. Pangal, J. C. Strum and S. Wagner Appl. Phys. Lett., 75(14), 1999, p. 2091.
- [71] M. Yamaguchi, K. Morigaki Journal of Non-Crystalline Solids, 137, 1991, p. 57.
- [72] A. H. Mahan, J. Yang, S. Guha and D. L. Williamson Phys. Rev. B, 61(3), 2000, p. 1677.
- [73] A. Barhdadi, H. Amzil, N. M'Gafad, T. Biaz, W. Eichhammer, J. C. Muller and P. Siffert Journal of Alloy and Compounds, 188, 1992, p. 221.