Uniformity Study of Amorphous and Microcrystalline Silicon Thin Films Deposited on 10cmx10cm Glass Substrate using Hot Wire CVD Technique

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The scaling up of the Hot Wire Chemical Vapor Deposition (HW-CVD) technique to large deposition area can be done using a catalytic net of equal spaced parallel filaments. The large area deposition limit is defined as the limit whenever a further increment of the catalytic net area does not affect the properties of the deposited film. This is the case when a dense catalytic net is spread on a surface considerably larger than that of the film substrate.

To study this limit, a system able to hold a net of twelve wires covering a surface of about 20 cm x 20 cm was used to deposit amorphous (a-Si:H) and microcrystalline (μ c-Si:H) silicon over a substrate of 10 cm x 10 cm placed at a filament-substrate distance ranging from 1 to 2 cm. The uniformity of the film thickness d and optical constants, $n(\mathbf{x}, \lambda)$ and $\alpha(\mathbf{x}, \hbar\omega)$, was studied via transmission measurements. The thin film uniformity as a function of the filament-substrate distance was studied. The experimental thickness profile was compared with the theoretical result obtained solving the diffusion equations. The optimization of the filament-substrate distance allowed obtaining films with inhomogeneities lower than $\pm 2.5\%$ and deposition rates higher than 1 nm/s and 4.5 nm/s for (μ c-Si:H) and (a-Si:H) respectively.

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1 Introduction Hot Wire Chemical Vapor Deposition (HW-CVD) is a very promising technique for the improvement of the microcrystalline silicon layer deposition involved in the production of micro-morph solar cells. The structural uniformity of the intrinsic microcrystalline (μ c-Si:H) silicon layer is crucial to preserve the efficiency of the cells when scaling the process to large deposition areas [1,2].

The standard PECVD technique is affected by the standing surface wave effect, which can compromise the uniformity of the film [3,4]. This fact makes it difficult to achieve high deposition rates (>1 nm/s) using the Very High Frequency (VHF) sources, and, simultaneously keep-

ing a low non-uniformity (< 5%) on the whole substrate [5,6].

The HW-CVD film's growth kinetic is governed exclusively by the diffusion of the different radical species created at the surface of the catalytic filament. This makes it much easier to scale up this technique to large area while maintaining the uniformity of the film [7,8]. Moreover, this technique has the potentiality to deposit μ c-Si:H material at very high deposition rate [9, 10].

In this work, the uniformity results of μ c-Si:H and *a*-Si:H films, deposited with a new HW-CVD system developed at the University of Barcelona, are reported. The purpose of the new design was to improve the films' unifor-

mity and deposition rate compared to the actual HW-CVD state of art.

Firstly, the model for the prediction of the deposition profile used during the design stage of the prototype is introduced. It will show that the only phenomenological parameter influencing the film's thickness profile, for a given wire configuration, is a length scale l. This leads to an uncertainty in the best filament to substrate distance d_{f-s} in order to minimize the film's inhomogeneity. For this reason, we deposited at different d_{f-s} to empirically optimise the homogeneity. The second section explains the experimental set up used for the deposition and the characterization of the samples. Finally, we show the obtained homogeneity results.

2 Design of the HW configuration The chemistry involved in the film's growth is very rich in radical species [11]. It includes the primary radicals Si and H, which are generated at the wire surface. Moving away from the filament these primary radicals start reacting with silane (SiH₄), arising new species involved in the process. Among them, SiH₃ is considered to be the most important in order to obtain high quality material. However, if the substrate is placed too far from the filaments, large radicals, are produced by secondary radical-radical reactions, which should be avoided. This simple schema justifies the existence of an optimal value, C, for the product

$$P_s \cdot d_{f-s} = C. \tag{1}$$

where P_s is the partial pressure of silane and C is a constant of the order of some cm·Pa. This argument is based on the fact that the probabilities of the different chemical reactions involved rely upon the value of C [12].

In the case of a wire net covering an infinite area, the deposition rate G can be raised following different strategies: increasing the filament temperature T_f , the catalyser surface S_c , and/or P_s . Thin wires of 0.15 mm diameter were used in our design in order to build a dense catalytic net, thus permitting to reduce as maximum as possible d_{f-s} while mantaining a reasonably low radiated power onto the substrate (1.5 W/cm²) for T_f =1850°C. Therefore, following Eq.(1) P_s can be considerably increased.

The model used to compute the film's profile assumes that the thickness $d(\mathbf{x})$, in the coordinate \mathbf{x} of the substrate, is proportional to the total flow of radicals $\mathbf{J}(\mathbf{x})$ reaching this point during the stationary regime of the deposition, i.e. $d \propto \mathbf{J}(\mathbf{x}) \cdot \mathbf{n}$, where \mathbf{n} is the unitary vector normal to the substrate plane. $\mathbf{J}(\mathbf{x}) = D\nabla c(\mathbf{x})$ is just a diffusion flow, being D the diffusion constant and $c(\mathbf{x})$ the radicals concentration. If we exclude the secondary radical-radical reactions, the total amount of radicals is preserved [12]. Hence, the stationary diffusion equation takes the form of the Poisson equation

$$\Delta c(\mathbf{x}) = \frac{\rho(\mathbf{x})}{D} \text{ for } \mathbf{x} \in \mathcal{S},$$
(2)

where $\rho(\mathbf{x}) = \partial c(\mathbf{x})/\partial t$ is the radicals generation rate at the wire surface. The domain of definition S was considered to be a parallelepiped, where a face was occupied by the substrate. Equation (2) is subject to Milne boundary conditions [13]

$$\mathbf{n} \cdot \nabla c(\mathbf{x}) = \frac{1}{l} c(\mathbf{x}) \text{ for } \mathbf{x} \in \partial \mathcal{S},$$
 (3)

with $l = 2\lambda(2 - \beta)/3\beta$ the characteristic length scale, where λ is the mean free path of the radicals and β is the sticking coefficient. Equation (2) has been solved using the images method [14]. The Milne boundary conditions, which are formally Robin type conditions, can be replaced by Dirichlet boundary conditions, $c(\mathbf{x}) = 0$, located at a distance *l* behind the boundary of the domain ∂S . This approximation is valid as long as *l* is small in relationship to the other length scales of the problem.

Figure 1 shows the level curves of the normalized thickness profile obtained by solving Eq. (2). The wire net is composed of 12 filaments of 19.5 cm length. The filaments are aligned parallel to the Y axis and the filament to filament distance was d_{f-f} =1.6 cm. l was estimated to be 0.4 cm, while the domain definition box S was defined by $(L_x, L_y, L_z) = (30, 20, 3.5)$ cm. d_{f-s} was fixed at 2 cm.



Figure 1 Normalized thickness profile obtained by solving the diffusion equation (2) for $d_{f-s} = 2$ cm. The thick continous line delimitates the area where thickness variations should be lower than $\pm 2\%$, while the 10 cm x 10 cm substrate area is delimitated by the dashed line.

3 Experimental details This work is focused on the optimization of the deposited μ c-Si:H and a-Si:H films homogeneity over an effective area of 10 cm x 10 cm using the aforementioned hot wire assembly of 12 tungsten filaments of 0.15 mm diameter and with a filament to filament

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distance $d_{f-f} = 1.6$ cm. For all the depositions, a base pressure of 10^{-4} Pa was considered low enough taking into account the aim of this study. Regarding the μ c-Si:H films, the deposition conditions were $T_s=275^{\circ}$ C, $T_f=1850^{\circ}$ C, $\Phi(\text{SiH}_4)=12 \text{ sccm}, \Phi(\text{H}_2)=188 \text{ sccm}, P=10 \text{ Pa}, \text{ with three}$ different filament to substrate distances ($d_{f-s}=1$, 1.5 and 2 cm) and a deposition time t_d =900 s. In the case of the a-Si:H films, the deposition conditions were $T_s=275^{\circ}$ C, $T_f=1850^{\circ}\text{C}, \ \Phi(\text{SiH}_4)=60 \text{ sccm}, \ \Phi(\text{H}_2)=140 \text{ sccm}, \ P=$ 10 Pa, with two different filament to substrate distances $(d_{f-s}=1.5 \text{ and } 2 \text{ cm})$ and $t_d=180 \text{ s}$. The optical transmission measurements were carried out with a home made experimental set-up. The light source covered a wavelength range from 400 nm to 1000 nm and the light was guided to the spectrofotometer via fiber optics. An X-Y table was used to scan the samples over an area of 170 mm x 170 mm with 1 mm step between measurements. The whole system was completely automatized. The well known Swanepoel envelope method [15] was used to determine the thickness and optical constants of the deposited films. However, for each scan, one measure with profilometer was necessary to fix the interference order.

4 Results and discussion



Figure 2 Thickness profile d along the x axis (centered at y=0) for five samples deposited with different filament to substrate distance $d_{f-s} = \{1, 1.5, 2\}$ cm, corresponding to the $\{\Delta, -, \circ\}$ markers. The thick lines show the results for the μ c-Si:H samples while the thinner continuos line those of the a-Si:H ones. The dashed thinner lines show the profiles obtained solving Eq. (2) with l=0.4cm.

4.1 Thickness uniformity Figure 2 shows the thickness profiles along the X axis while Y=0 of the five sam-

ples studied in this work. The X direction is transversal to the orientation of the hot wires, for this reason is the most interesting to be studied. It shows that, for d_{f-f} bigger than d_{f-s} , small variations of the substrate position lead to strong changes in the film thickness profile. However, the thickness profiles predicted by the diffusional model show good agreement with the measurements. The deposition rates for all samples were higher than 1 nm/s and 4.5 nm/s for the μ c-Si:H and a-Si:H material respectively.

Figure 3 shows the absolute thickness deviations along the X axis for the μ c-Si:H samples. For values of d_{f-s} smaller than 2 cm the thickness variations are correlated with the filaments positions, but if we move further, this correlation is lost. Particularly, for $d_{f-s}=2$ cm the strongest inhomogeneities factors are others, because at this distance the substrate can be considered already subject to a plane radicals front with variations smaller than $\pm 1\%$, see Fig. 1.



Figure 3 Absolute thickness deviation profile Δd along the x axis (centered at y=0) for three μ c-Si:H samples deposited with different filament to substrate distance $d_{f-s} = \{1, 1.5, 2\}$ cm, corresponding to the $\{\Delta, -, \circ\}$ markers.

Hence, the smallest distance to obtain an uniform layer, is $d_{f-s} = 2 \operatorname{cm} \approx 5/4 d_{f-f}$. Our ratio $d_{f-s}/d_{f-f} \approx 5/4$ is much smaller than those found by [8], i.e. $d_{f-s}/d_{f-f} \approx 2$, which was probably not working in the large area limit.

The complete thickness map obtained for the sample deposited at this distance is showed in Fig. 4. The thickness inhomogeneity affecting the 10 cm x 10 cm area of interest is lower than $\pm 2.5\%$. This is slightly higher than what predicted solving the diffusion equation (Fig. 1).

4.2 Optical constants uniformity To study the homogeneity of the optical constants $n(\mathbf{x}, \lambda)$, and, $\alpha(\mathbf{x}, \hbar\omega)$, determined via transmission measurement, the average deviation of these quantities, defined by $\Delta q(\mathbf{x}) = 1/T \int |q(\mathbf{x}, r) - \bar{q}(r)|/\bar{q}(r)dr$ were computed, where r corresponds to λ , or, $\hbar\omega$ respectively. T is the length of the integration interval: $\lambda \in [650, 850]$ nm for $n(\lambda)$ and $\hbar\omega \in [1.5, 1.9]$ eV for $\alpha(\hbar\omega)$. The mean function values $\bar{q}(r)$ were evaluated on the 10 cm x 10 cm area of interest.



Figure 4 Thickness profile, in nm, of a μ c-Si:H sample with $d_{f-s} = 2$ cm. The thick continuos line delimitates the area where thickness variations are lower than $\pm 2.5\%$, while the 10 cm x 10 cm substrate area is delimitated by the dashed line.



Figure 5 Profile of the average deviation of the optical constant $n(\lambda)$ and $\alpha(\hbar\omega)$ along the x axis (centered at y=0) for three μ c-Si:H samples deposited with different filament to substrate distance $d_{f-s} = \{1, 1.5, 2\}$ cm, corresponding to the $\{\Delta, -, \circ\}$ markers.

Figure 5 shows the profile of the average deviation Δn , and, $\Delta \alpha$ for the μ c-Si:H samples deposited with different filament to substrate distance. The average deviation of both constants decreases when the filament to substrate distance d_{f-s} is increased. This behavior is in agreement with the trend observed for the thickness deviation.

5 Conclusion In this work we presented the obtained results concerning the optimization of the samples homogeneity deposited with the new HW-CVD net configuration developed at the university of Barcelona. Our approach of building a dense net of thin wires of 0.15mm diameter, permits depositing very uniform films, with an inhomogeneity lower than $\pm 2.5\%$, at very high deposition rate (> 1nm/s for μ c-Si:H and > 4.5 nm/s for a-Si:H), mantaining relatively low the temperature of the substrate, $T_s \approx 275^{\circ}$ C. The future confirmation of the possibility to deposit high quality material, combined with the facility to scale up this design to industrial area, would prove the validity of this system for the deposition of the intrinsic μ c-Si:H layer for the production of micro-morph solar cells.

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References

- L. Li, Y.M. Li, J.A.A. Selvan, A.E. Delahoy, and R.A. Levy, Journal of Non-Crystalline Solids 347, 106 (2004).
- [2] B. Rech, T. Roschek, T. Repmann, J. Muller, R. Schmitz, and W. Appenzeller, Thin Solid Films 2003 427, 157 (2003).
- [3] M.A. Lieberman, J.P. Booth, P Chabert, JM Rax, MM Turner. Plasma Sources Science and Technology 11, 283 (2002)
- [4] L. Sansonnens, A. Pletzer, D. Magni, A.A. Howling, C. Hollenstein, J.P.M Schmitt, Plasma Sources Science and Technology 6,170 (1997).
- [5] B. Strahm, C. Hollenstein, and A. A. Howling, Prog. Photovolt: Res. Appl. 16 687 (2008).
- [6] B. Rech, T. Repmann, S. Wieder, M. Ruske, U. A. Stephan, Thin Solid Films 2006 **502** 300 (2006).
- [7] K. Ishibashi, M. Karasawa, G. Xu, N. Yokokawa, I. Manabu, A. Masuda, and H. Matsumura, Thin Solid Films 430 58 (2003).
- [8] A. Ledermann, U. Weber, C. Mukherjee, B. Schroeder, Thin Solid Films 395 61 (2001).
- [9] J. Cifre, J. Bertomeu, J. Puigdollers, M. Polo, J. Andreu, and A. Lloret, Appl. Phys. A: Mater. Sci. Process. 59 645 (1994).
- [10] R.E.I. Schropp, Y. Xu, E. Iwaniczko, G.A. Zaharias, and A.H. Mahan, Material Research Society Symposium Proceeding, vol. 715, p. A26, (3.1). (2002)
- [11] E. C. Molenbroek, A. H. Mahan, and E. J. Johnson, J. Appl. Phys. **79** (9) 7278-7292 (1995)
- [12] E. C. Molenbroek, A. H. Mahan, and Alan Gallagherb, J. Appl. Phys. 82 (4) 1909 (1997).
- [13] A. Gallagher, J. Appl. Phys. 60 (4) 1369 (1986)
- [14] D. Gilbarg and N.S. Trudinger, Elliptic Partial Differential Equations of Second Order, Springer- Verlag, Berlin, 1977.
- [15] R. Swanepoel Journal of Physics E-Scientific instruments 16, 1215 (1983).