

Low temperature (<100 °C) fabrication of thin film silicon solar cells by HWCVD

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Abstract

Amorphous silicon films have been made by HWCVD at a very low substrate temperature of ≤ 100 °C (in a dynamic substrate heating mode) without artificial substrate cooling, through a substantial increase of the filament–substrate distance (~ 80 mm) and using one straight tantalum filament. The material is made at a reasonable deposition rate of 0.11 nm/s. Optimized films made this way have device quality, as confirmed by the photosensitivity of $> 10^5$. Furthermore, they possess a low structural disorder, manifested by the small $I/2$ value (half width at half maximum) of the transverse optic (TO) Si–Si vibration peak (at 480 cm^{-1}) in the Raman spectrum of ~ 30.4 cm^{-1} , which translates into a bond angle variation of only $\sim 6.4^\circ$. The evidence gathered from the studies on the structure of the HWCVD grown film by three different techniques, Raman spectroscopy, spectroscopic ellipsometry and transmission electron microscopy, indicate that we have been able to make a photosensitive material with a structural disorder that is smaller than that expected at such a low deposition temperature.

Tested in a p–i–n solar cell on Asahi SnO_2 :F coated glass (without ZnO at the back reflector), this i-layer gave an efficiency of 3.4%. To our knowledge, this is the first report of a HWCVD thin film silicon solar cell made at such a low temperature.

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1. Introduction

The recent trend in the fabrication of devices on plastics has opened a wide variety of applications. Thin film silicon solar cells that could be used as power supplies for these devices need to be developed at a low temperature of ≤ 100 °C (which is compatible for most of the plastics such as PEN, PES and many types of PET). However, deposition of amorphous silicon (a-Si:H) at temperatures lower than 200 °C usually leads to increased structural disorder and defects in the material [1], owing to lowering of the diffusion length of the precursors on the growing surface. A systematic increase in the Urbach edge parameter [2], an increase in the line width of the TO mode of the Si–Si vibration detected in the Raman spectrum [2,3], and an increase in the disorder parameter obtained from the ellipsometry [4] measurement with decreasing substrate temperature confirm this hypothesis.

To address this challenge, we are investigating hot-wire chemical vapour deposition (HWCVD, also called Cat-CVD) as an alternative technique to PECVD for the deposition of intrinsic a-Si:H layers for the application in solar cells. This technique offers three advantages: (i) HWCVD is an *ion free deposition* technology, that would, among others, ensure powder free deposition, (ii) a-Si:H and silicon nitride films made by HWCVD have far *less stress* than those made by PECVD [5], (iii) a high flux of atomic H is generated in HWCVD which may help to remove highly strained bonds and decrease the disorder.

2. Experimental

All the intrinsic a-Si:H layers for this research were grown in the ATLAS (Apparatus for Thin Layers of Amorphous Silicon), a single high vacuum chamber along with a load lock chamber. The ATLAS is a system designed for the study of the growth of silicon thin films in situ by kinetic and spectroscopic ellipsometry. It is fitted with a hot-wire assembly that consists of Tantalum (Ta) wires, which are hooked up to an electrical circuit, and a shutter which shields the substrate from the wires.

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The shutter is opened to start the deposition. In this case we are using hydrogen gas (H_2) and silane (SiH_4) with a hydrogen to silane ratio of 20.

In order to do low temperature depositions the HW-assembly of the ATLAS had to be modified. In order to decrease temperature we increased the distance between the filament and substrate and fixed it at 80 mm. We also did a number of temperature measurements on the front side of a glass substrate at different filament currents and different heater temperatures. This was done using a thermocouple.

The doped thin film silicon layers were made by VHF-PECVD in our ultra high vacuum multichamber system called ASTER. These doped layers at low temperatures have already been developed for complete VHF-PECVD low temperature cells [6]. Thus, while making a p–i–n cell there were air breaks (twice) between the deposition of the doped layers and the i-layer. Solar cells were made on an Asahi U-type SnO_2 coated glass substrate in a superstrate configuration; glass/ SnO_2 /p–a–Si:H(VHF-PECVD)/i–a–Si:H(HWCVD)/n–a–Si:H(VHF-PECVD)/Ag/Al. Current–Voltage (I – V) measurements were done under AM1.5 100 mW/cm^2 light condition with a WACOM dual beam solar simulator at a controlled temperature of 25 °C.

The ellipsometry data obtained for the samples on Corning 1737F glass in the range of 1.5 to 5 eV were analysed with Tauc–Lorentz model. From the parametric modelling we obtained the dielectric function, thickness and roughness parameter. Raman spectroscopy of samples on glass was done in a backscattering geometry using an Ar ion laser at a wavelength of 514.5 nm. Cross sectional transmission electron microscopy (XTEM) was done in a defocused condition to detect the void structure. In this article we have compared the characteristics of the HWCVD a–Si:H film with two other films; (1) VHF-PECVD a–Si:H made at 100 °C with $H_2/SiH_4=5$ at a deposition rate of 0.13 nm/s, and (2) VHF-PECVD a–Si:H made at 200 °C with $H_2/SiH_4=1$ at a deposition rate of 2 nm/s.

3. Results and discussion

3.1. Material properties

Fig. 1 shows the substrate temperature of the HWCVD assembly after the shutter is opened (the filaments are already

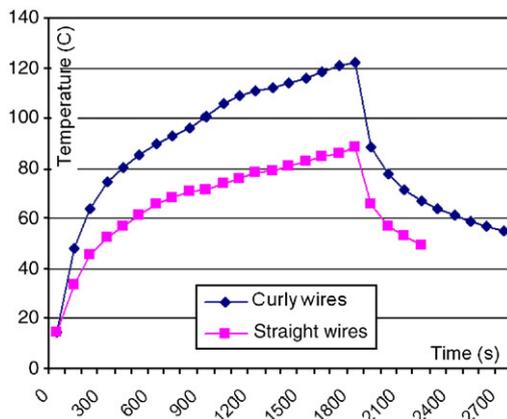


Fig. 1. The effect of effective filament length on substrate temperature.

Table 1

Optoelectronic and structural characteristics of HWCVD and VHF-PECVD a–Si:H samples on glass made at $T_{sub} \leq 100$ °C

a–Si:H	HWCVD	VHF PECVD
σ_d ($\Omega^{-1} cm^{-1}$)	2.48×10^{-11}	4.5×10^{-12}
σ_{ph}/σ_d	1.06×10^5	1.7×10^5
E_a (eV)	0.82	0.85
n (600 nm)	4.05	4.16
H_2/SiH_4	20	5
$\Gamma/2$ (Si–Si TO peak $480 cm^{-1}$)	30.4	31.9
R_d (nm/s)	0.11	0.13
E_{04} (eV)	1.95	2.05

hot). It can be observed that with a straight wire the temperature that is reached in 30 min is less than 100 °C, whereas with a curled wire the temperature reaches 120 °C. This is the approximate time needed for the deposition of an i-layer used in our cell (~ 350 nm). It also shows that during the dynamic state of substrate heating, the initial depositions are at temperatures much lower than 100 °C.

Table 1 shows the optoelectronic properties of the intrinsic amorphous silicon layers made by HWCVD in the dynamic heating mode. A photosensitivity of $>10^5$ confirms the device quality of materials. We attribute this high quality of the HWCVD material to a considerable amount of atomic hydrogen generated in the HWCVD process. Fig. 2 shows the Raman spectrum of this material along with two other samples for comparison. These three samples are (1) HWCVD a–Si:H made at 100 °C with $H_2/SiH_4=20$, (2) VHF-PECVD a–Si:H made at 100 °C with $H_2/SiH_4=5$ and (3) VHF-PECVD a–Si:H made at 200 °C with $H_2/SiH_4=1$. It clearly shows that there is no crystalline fraction (no peak near $520 cm^{-1}$). The transverse optic (TO) Si–Si vibration peak in the Raman spectrum at $480 cm^{-1}$ shows a very small FWHM ($\sim 60.8 cm^{-1}$) value for the HWCVD material. The FWHM of both the VHF-PECVD layers are $\sim 2 cm^{-1}$ wider than the HWCVD sample. The error in the line width is $\pm 0.2 cm^{-1}$. We observe no increase in the FWHM for the low temperature deposited HWCVD material compared to either the low temperature VHF-PECVD material or the standard device quality amorphous silicon made at high

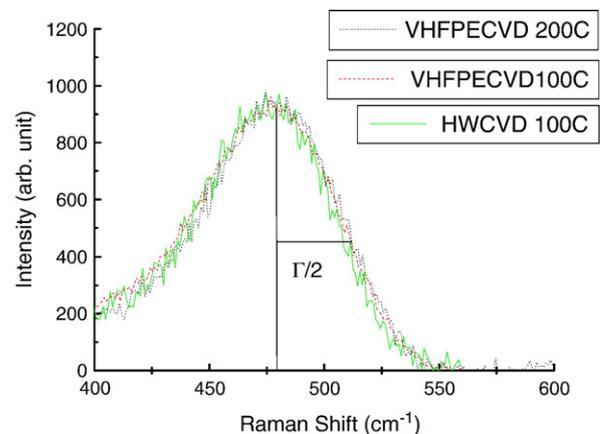


Fig. 2. Raman spectra showing the Si–Si TO peak of three types of a–Si:H samples.

Table 2
Output parameters of the simulation of spectroscopy ellipsometry data

Sample	<i>d</i> (nm)	<i>E_g</i> (eV)	<i>E₀</i> (eV)	<i>A</i>	<i>C</i>
HWCVD 100 °C	289.8±2.0+10.6 (roughness)	1.745	3.615	181.8	1.671
VHF-PECVD 100 °C	197.6±0.55+4.7 (roughness)	1.721	3.618	205.7	2.10
PECVD 100 °C [4]	198.5	1.65	3.66	201	2.39

temperature (200 °C). The half width at half maximum (shown as $\Gamma/2$ in the figure) has been related to the root mean square of bond angle distribution. We have used here the relation given by Beeman et al. [7],

$$\frac{\Gamma}{2} = 3.2\Delta\Theta + 7.4 \tag{1}$$

which gives a low bond angle variation of $\sim 6.4^\circ$ for the HWCVD material. Our results are at variance with the earlier reports where a lowering of deposition temperature, keeping other process parameters constant, invariably led to a systematic increase in the FWHM or the disorder in the film [2,3]. Further evidence of the low disorder in the low temperature deposited HWCVD made material comes from the spectroscopic ellipsometry (SE) studies presented below.

Generally, the Bruggemann effective medium approximation (BEMA) is used to simulate the dielectric function of a mixed phase material containing an amorphous matrix, voids and crystalline components. However, the BEMA is effective when the dielectric function of the constituents is well defined and it is less accurate when the material contains significant hydrogen content because the effect of hydrogen is generally omitted. The difficulty in the independent determination of the dielectric function of the individual inclusions leads to an erroneous fitting of the dielectric function. Sometimes a crystalline fraction is obtained through modelling while the Raman spectra do not show any such crystalline component. This discrepancy has been explained by a few reports by invoking paracrystallinity in the material [8]. The other approach to simulate the dielectric function is by using the dispersion law, where the dielectric function is described by the Tauc–Lorentz dispersion law. The TL model has shown excellent fitting of the dielectric function [4].

The imaginary part of the dielectric function in a TL model is described as,

$$\epsilon_{im}(E) = \frac{A \cdot E_0 \cdot C \cdot (E - E_g)^2}{(E^2 - E_g)^2 + C^2 \cdot E^2} \cdot \frac{1}{E} \quad E > E_g \tag{1}$$

$$\epsilon_{im}(E) = 0 \quad E \leq E_g \tag{2}$$

where E_0 is the peak transition energy and E_g is the gap energy and C is a broadening parameter, which can be related to the disorder in the material and A is related to the film density. The order in the material made at various temperatures and dilution conditions has been correlated with the C parameter [4] and a systematic increase of the C parameter from an optimum value of ~ 2.16 for a device quality amorphous silicon made at 250 °C

to a value of 2.44 deposited at 50 °C has been observed [4]. Data in [4] have been obtained using the TL model as well and the same simulation process and the model are used both in that article as well as for our SE data given in this article. This enables a fair comparison of the output data in this paper with the data in [4]. We have fitted the dielectric function of two amorphous silicon samples, (i) HWCVD a-Si:H made at 100 °C and (ii) VHF-PECVD a-Si:H made at 100 °C. The SE data are analysed taking into account the substrate, the thin film bulk and its surface roughness. The dielectric function of the substrate (Corning 1737F) is known from the SE measurements performed before deposition. The surface roughness is considered as an overlayer formed by a mixture of 50% bulk material and 50% voids and it should be noted that the roughness data derived from the ellipsometry should not be directly correlated with geometrical roughness obtained from XTEM. The thin film bulk is described by the TL model as described above.

Table 2 shows the fitting parameters of the ellipsometry data. It can be clearly observed that the C parameter of the VHF-PECVD material can be well compared to the device quality a-Si:H material made at 250 °C reported in [4]. The HWCVD material had a much smaller C value of ~ 1.67 . We do not have the complete explanation of such a low C -value, neither have we been able to account for the inhomogeneity of the film along the growth axis. The low value of C , which is an average value for bulk, might suggest that the low temperature deposited material by HWCVD shows a better order than that normally expected at such temperatures.

Further correlation with the transmission electron microscopy is in progress. Preliminary XTEM results show a structure with elongated voids along the growth direction (Fig. 3) similar to the structure reported in the literature on protocrystalline Si materials made at higher temperature (250 °C) [9]. The elongated voids are 10–40 nm long and 1–5 nm wide. The first 35 nm however does not contain any voids. The following 125 nm contains a void fraction estimated as $(3.5 \pm 1) \cdot 10^{-4}$. The top half of the layer contains a void fraction of $(1.2 \pm 0.5) \cdot 10^{-4}$. The average is roughly $(2 \pm 0.7) \cdot 10^{-4}$.

Though the presence of such a void structure itself does not prove the ordering in the structure, we are tempted to compare the existence of elongated voids in this layer with that in proven

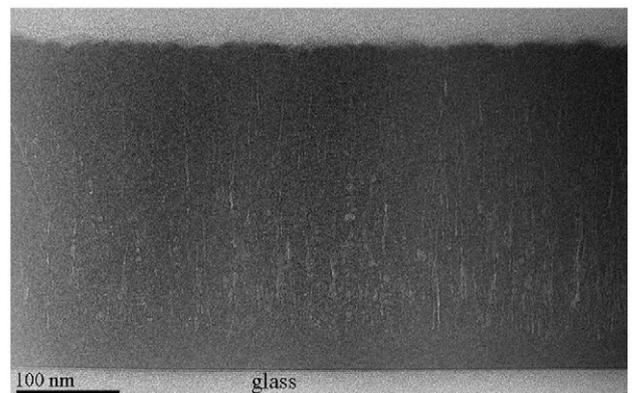


Fig. 3. XTEM image of a HWCVD a-Si:H made at 100 °C.

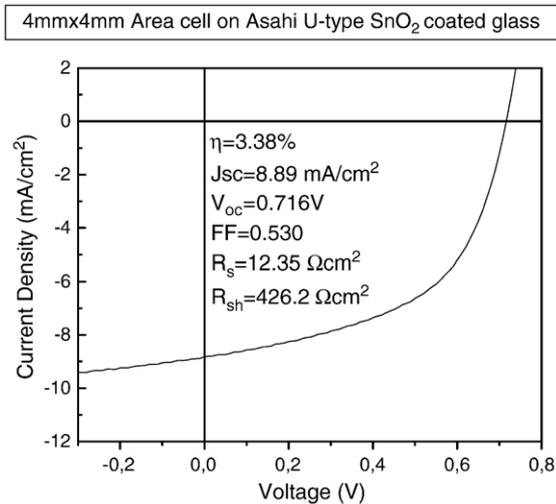


Fig. 4. I – V characteristics of an HWCVD a-Si:H solar cell made at $<100^\circ\text{C}$ on Asahi U-type TCO substrate.

protocrystalline materials as reported in the literature [9]. Once again, it appears that the presence of voids is not an indication of inferior electronic quality. Details of the correlation with the structure, especially the high-resolution micrograph image will be published elsewhere.

A possible explanation for the high structural order and device quality for our amorphous silicon films made at such low substrate temperature may be the deposition with long filament to substrate distance, due to which reactive (such as SiH₂) and heavy silicon radicals have less probability in reaching the growing surface. These sorts of radicals have low diffusion coefficient on the growing surface and at low deposition temperatures, due to substantial lowering of diffusion length of these species on the growing surface, they can induce disorder in the film. Further work is needed to verify this hypothesis.

3.2. Solar cell

Fig. 3 shows the I – V characteristics of a p–i–n solar cell on an Asahi TCO substrate implementing this HWCVD grown a-Si:H i-layer. The back contact was simple silver/aluminium (no ZnO/Ag back reflector was used). The efficiency is 3.4%. The high optical band edge ($\sim E_{04}$ of 1.95 eV) of the intrinsic a-Si:H layer and the absence of a back reflector had a strong limiting effect on the current density, which is 8.89 mA/cm^2 . The V_{oc} and FF (0.716 V and 0.530, respectively) may have been affected by the thickness

dependence of the layer properties due to (i) the deposition in the dynamic heating state that gives non-optimum material at the front side of the cell (lower deposition temperature), where the highest carrier generation density is located when a cell is made in the superstrate structure and (ii) the two air breaks between the doped layers and the intrinsic layer. We speculate that a cell made in an n–i–p configuration will be less sensitive to this temperature effect as in that case the i-layer near the p/i interface (which is most sensitive for solar cell performance) will have better electronic property due to deposition at a relatively higher temperature (Fig. 4).

4. Conclusion

At a temperature less than 100°C amorphous silicon films with high photosensitivity and a remarkably low structural disorder (considering the low deposition temperature) have been made by HWCVD. A p–i–n solar cell on an Asahi U-type substrate implementing this i-layer delivered 3.4% efficiency (without ZnO layer at the back reflector).

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