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Thin film silicon devices deposited at 100 °C: A study on the structural order of the photoactive layer

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Abstract

The dielectric functions of thin film silicon materials on glass were measured by spectroscopic ellipsometry (SE) and simulated by using the Tauc-Lorentz (TL) dispersion law, which provided information on disorder (C) and density (A). A VHF plasma-deposited sample made at 100 °C with an optimum hydrogen dilution shows density (relative packing density of Si–Si bonds as estimated by SE) and structural disorder that are comparable to samples made at 200 °C. HWCVD materials made at 100 °C at lower hydrogen dilution conditions have a less dense structure and higher roughness compared to the plasma-deposited samples. This can be attributed to the absence of ion bombardment on the growing film. Out of all samples investigated, the HWCVD sample made at a hydrogen to silane flow ratio value of 20 showed a remarkably low structural disorder ($C = 1.67$) even though the deposition temperature was only 100 °C. A small bond angle variation of ~6.4° as determined from its Raman spectrum, the presence of small (1–1.5 nm) dispersed crystalline-like islands in the silicon matrix, and sharp rings in the selective area diffraction pattern point towards a special ordered structure. The photoresponse of this material is $>10^5$.
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1. Introduction

Fabrication of thin film silicon devices on cheap plastics requires deposition processes at temperatures lower than 100 °C where a standard PECVD of amorphous silicon (a-Si:H) usually leads to increased structural disorder and defects in the material [1]. By optimizing the hydrogen to silane flow ratio (R) for the deposition of i-layers, we thus far have made solar cells at 100 °C on Asahi TCO substrates in the p–i–n configuration with efficiencies of 7.3% [2] by very high frequency plasma enhanced chemical vapor deposition (VHF PECVD) and 3.4% [3] by hot-wire CVD (HWCVD). The purpose of this paper is to study the structural order of the materials that are optimum for solar cell application.

2. Experimental

2.1. Depositions

All the depositions of silicon thin films (Table 1) were done in ultra high vacuum deposition systems. The VHF PECVD samples were made at an RF frequency of 50 MHz in the deposition system called ASTER [4]. The substrate temperature was controlled by the set temperature of the heater. The HWCVD samples were made in a deposition system called ATLAS [3] at a very low substrate

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Table 1
Parameters obtained from the simulation of the ellipsometry data

Process	T (°C)	R	σ_{SE} (nm)	E_g (eV)	A	E_o (eV)	C
RF PECVD[a] [6]	100	Pure silane		1.65	201	3.66	2.39
RF PECVD[a]	100	Pure silane	4.9	1.74	194	3.69	2.38
VHF PECVD[b]	100	20	4.7	1.72	206	3.62	2.10
HWCVD	100	7.5	14.4	1.85	154	3.77	2.25
HWCVD	100	10	13.2	1.78	155	3.7	2.26
HWCVD[b]	100	20	10.6	1.75	182	3.62	1.67
HWCVD	100	30	8.8	1.83	214	3.68	2.08
VHF PECVD	200	1	10.5	1.72	216	3.42	2.02
RF PECVD[a]	200	Pure silane	4.3	1.64	209	3.62	2.27
RF PECVD[a] [6]	200	Pure silane		1.66	216	3.62	2.29

R: H_2/SiH_4, σ_{SE}: Surface roughness (ellipsometry), E_g: band gap, E_o: oscillator peak energy.
[a] 13.56 MHz frequency.
[b] The optimized layers used in solar cells [3].

temperature of ⩽100 °C (in a dynamic substrate heating mode) without artificial substrate cooling. The HWCVD assembly consists of a tantalum filament with 0.5 mm thickness, which was heated to a temperature of ~1800 °C. By keeping a high substrate to filament distance of 8 cm and using only a single straight wire, a temperature of ⩽100 °C could be maintained at the substrate [3]. For all of the above depositions a gas mixture of silane and hydrogen was used as process gas. A few PECVD samples made from pure silane at the standard frequency of 13:56 MHz in a deposition system called PASTA were used as reference samples.

2.2. Characterization

All the optical measurements were made on samples deposited on Corning 1737F glass substrates. Spectroscopic ellipsometry (SE) measurements were made in the spectral range of 1.5–5 eV at room temperature using a Jobin-Yvon UVISEL spectroscopic phase-modulated ellipsometer. The dielectric functions obtained by SE of the thin film silicon materials on glass have been simulated by using the Tauc-Lorentz (TL) dispersion law [5,6]. Raman spectra were recorded in a backscattering geometry using 514.5 nm light from an argon ion laser and a triple monochromator. The cross sections of the different layers were prepared for TEM by first gluing a glass slide on the film side of the material, then cutting a cross section with a thickness of 0.5–1 mm with a diamond saw, mechanically grinding and polishing the cross section to a thickness of ~10 μm, putting a piece of the cross section on a Cu slot grid and thinning to electron transparency using a Gatan PIPS 691 ion mill, using Ar. CM30T and CM30UT Philips transmission electron microscopes (300 kV) were used for imaging. Different types of images were taken. For bright field (BF) images, the undiffracted beam is selected to make a diffraction contrast image. For high-resolution electron microscopy (HREM) the central beam is used together with diffracted beams to form an image of the specimen. With a suitable beam direction and resolution, atomic planes or atomic columns can be made visible. For selected area diffraction pattern (SADP), the diffraction pattern is obtained of an area chosen with an aperture.

3. Results and discussion

Hydrogen dilution of silane was needed to obtain the best optoelectronic properties for both VHF PECVD as well as HWCVD samples. Whereas the best VHF PECVD layer was made at hydrogen to silane flow ratio (R) of 5, a comparatively higher R of 20 was needed for the best HWCVD film, though both these films have similar deposition rate (respectively, 0.13 and 0.11 nm/s) and photosensitivity ($>10^5$) [3]. However, we see interesting differences in their structural properties and in the way the structure varies with hydrogen dilution.

We have used basically three techniques to analyze the structure of the films and this paper will make a correlation between the data from these techniques to arrive at a conclusion regarding the structural order and its sensitivity to the deposition conditions.

3.1. Raman spectroscopy

The Si–Si transverse optic (TO) vibration peak in the Raman spectrum gives first evidence of the improvement in the structural order of the HWCVD deposited material with hydrogen dilution. Fig. 1 shows the $\Gamma_{1/2}$ values (half width at half maximum) of the TO peak centered at 480 cm^{-1}, which is assigned to the amorphous type structure. We have not observed any crystalline peak (520 cm^{-1}). The $\Gamma_{1/2}$ reaches a minimum at a H_2/SiH_4 flow ratio of 20. The bond angle variation was calculated using the relation

$$\frac{\Gamma(cm^{-1})}{2} = 3.2\Delta\Theta(^\circ) + 7.4, \quad (1)$$

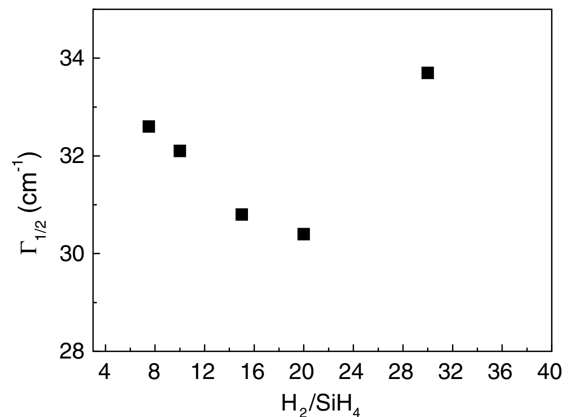


Fig. 1. Dependence of half width at half maximum of the amorphous Si–Si TO peak of the Raman spectrum on the deposition parameter hydrogen to silane flow ratio for HWCVD deposition.

where $\Delta\Theta$ is the bond angle variation, expressed in degrees (°) and $\Gamma_{1/2}$ is expressed in cm^{-1}. For the sample with H_2/SiH_4 flow ratio of 20 the bond angle variation is only 6.4°.

3.2. Spectroscopy ellipsometry

The dielectric functions obtained by spectroscopic ellipsometry (SE) of the thin film silicon materials on glass have been simulated by using the Tauc-Lorentz dispersion law [5,6]. The imaginary part of the dielectric function in a TL model is described as

$$\varepsilon_{im}(E) = \frac{A \cdot E_0 \cdot C \cdot (E - E_g)^2}{(E^2 - E_g)^2 + C^2 \cdot E^2} \cdot \frac{1}{E} \quad \text{for } E > E_g, \tag{2}$$
$$\varepsilon_{im}(E) = 0 \quad \text{for } E \leqslant E_g,$$

where E_0 is the peak transition energy, E_g is the gap energy, C is a broadening parameter, which is related to the disorder in the material and A is related to the film density [6]. We have fitted the dielectric function of three types of amorphous silicon samples, made at 100 °C by (i) HWCVD (ii) VHF-PECVD and (iii) standard RF PECVD (13.56 MHz), and (iv) two standard a-Si:H samples made at 200 °C as reference. The SE data are analyzed taking into account the substrate, the thin film bulk and its surface roughness, which is regarded as an over-layer formed by a mixture of 50% bulk material and 50% voids [7].

Table 1 shows the fitting parameters of the ellipsometry data. As a reference, the C and A parameters of our device quality 13.56 MHz PECVD samples deposited at 200 °C are comparable to literature values [6] and significantly smaller than those of 100 °C 13.56 MHz PECVD samples, confirming the effect of substrate temperature on the structural order. We observe that this is also the trend for VHF PECVD samples; however at both temperatures the structural order in VHF PECVD samples is much better than that of the 13.56 MHz PECVD samples. The VHF sample made at 100 °C using an optimum H_2 dilution shows density and structural order that are even better than the device quality a-Si:H sample made by RF PECVD at 200 °C. The HWCVD materials made at low hydrogen dilution conditions have a less dense structure and higher roughness compared to the plasma-deposited samples. Among all samples considered, it is observed that the C parameter reaches the lowest value ($C = 1.67$) for the HWCVD sample made at an optimum R value of 20, even though it was made at only 100 °C. This material also shows the best device quality with a photoresponse of $>10^5$. The Raman spectra of these samples also confirm this high structural order [3]. The samples marked with asterisk in Table 1 are the optimized i-layers used in the solar cells made at 100 °C. An interesting observation is that the structural parameters of these samples made at similar substrate temperature of ~100 °C, similar deposition rates and similar deposition pressure conditions of ~0.1 mbar, show quite different characteristics. The VHF PECVD sample is more dense, whereas the HWCVD sample has a lower structural disorder.

3.3. Cross-sectional transmission electron microscopy (XTEM)

XTEM images of the optimized films (asterisk in Table 1) show the basically amorphous nature of all the films. Selective area diffraction pattern of the films show rings that confirm the amorphous nature, though the sharpness of the rings indicated a better structural order than a typical amorphous network. However, we could not see a significant difference in the SADP patterns between the best HWCVD and the VHF PECVD samples made at 100 °C (marked with asterisks in Table 1). This indicates that on a macro scale the matrixes are similar and basically amorphous. There are however, a few significant differences: (1) The HWCVD sample shows narrow (~1.5 nm width) and elongated voids (along the growth direction) which starts after incubation of a compact phase of 35 nm, whereas the VHF PECVD sample show a rather compact structure without voids [8]. In addition the HWCVD film also shows some spherical voids. The relatively void-rich nature of the HWCVD films goes along with the behavior of the A parameters. The elongated, not interconnected, void structure has earlier been observed in protocrystalline silicon type of HWCVD materials made at 250 °C [9]. The HREM of the HWCVD sample also shows dispersed tiny highly ordered regions (lattice fringes) of around ~1–1.5 nm (Fig. 3). In the fast Fourier transform (FFT) of the HREM image, we do not observe any reflection plane, but it shows asymmetry. A circular symmetry (see reference FFT, shown in bright contrast), would indicate that the frequency of structure occurs in all directions with equal

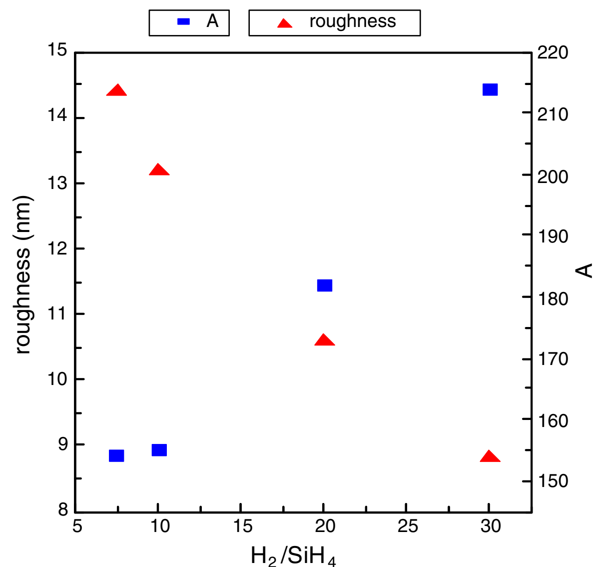


Fig. 2. Dependence of roughness and parameter A determined from the ellipsometry analysis on deposition parameter hydrogen to silane flow ratio for HWCVD deposition.

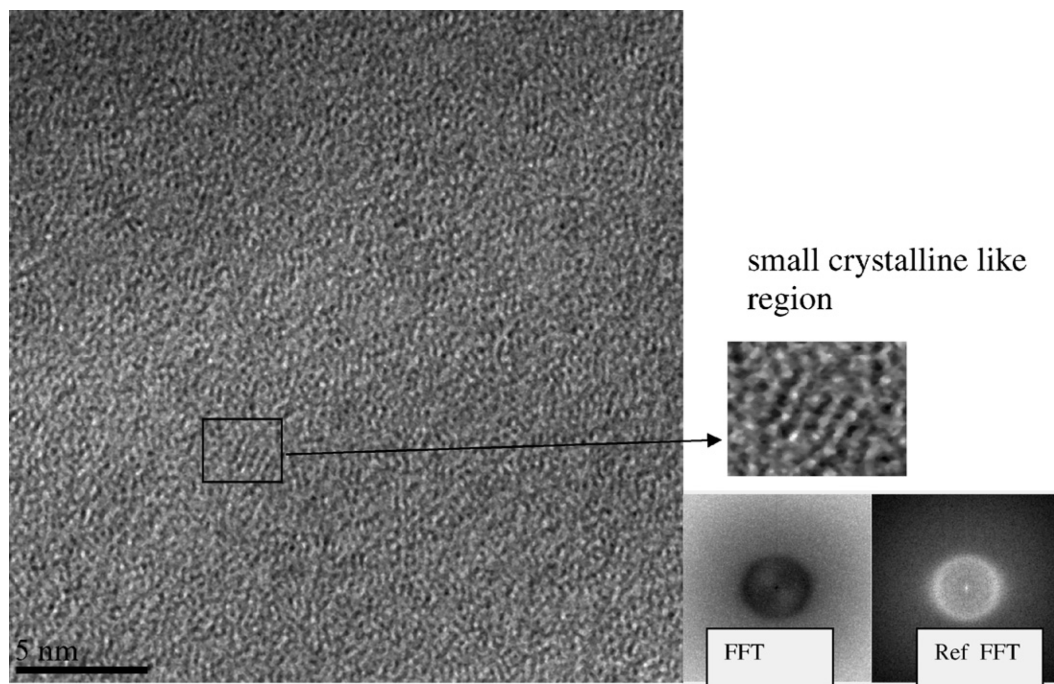
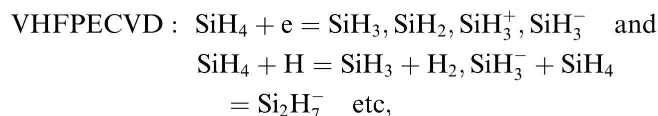


Fig. 3. High resolution transmission electron micrograph of the HWCVD a-Si:H sample made at 100 °C with H_2/SiH_4 of 20. The fast Fourier transform (FFT) of the image shows more order than a typical amorphous network.

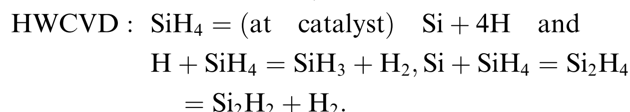
preference and the asymmetry ring for the HWCVD film means that the preferred frequency occurs mostly in a certain direction or that the structural order proceeds in a preferential direction.

The above three structural analyses, in general, show consistency. All the samples that have been studied show amorphous character, though they also show relaxed structures with optimum hydrogen dilution. A HWCVD sample at high dilution (see Table 1 for $R = 30$) was further studied by spectroscopic ellipsometry at decreasing thickness (by successive etching steps), but no indication of crystalline fraction could be found. The low density and high roughness of HWCVD samples at low hydrogen dilution conditions can be attributed to the absence of ion impact on the growing film [10]. However, the compactness of the film can also be controlled by the impinging atomic hydrogen. This aspect was clearly observed for the case of HWCVD samples (Fig. 2). The A parameter of HWCVD samples is continuously improved with increasing dilution, with concomitant decrease of roughness. The origin of elongated voids (after an incubation phase) in the optimized HWCVD film suggests the release of internal stress in the film though the creation of voids when a critical stress level is reached and this leads to a relaxed network, manifested in a small C value. This mechanism was suspected earlier with reference to the optimized protocrystalline silicon HWCVD films made at 250 °C [9].

The disorder in a material depends on the growth processes at the growing surface, which in turn depends on the substrate temperature, the type of deposition species, and their abundance relative to the atomic hydrogen flux. Gas phase chemistries of the two processes are given below.



$$\text{VHFPECVD}: \ SiH_4 + e = SiH_3, SiH_2, SiH_3^+, SiH_3^- \quad \text{and} \quad SiH_4 + H = SiH_3 + H_2, SiH_3^- + SiH_4 = Si_2H_7^- \quad \text{etc},$$



$$\text{HWCVD}: \ SiH_4 = (\text{at} \quad \text{catalyst}) \quad Si + 4H \quad \text{and} \quad H + SiH_4 = SiH_3 + H_2, Si + SiH_4 = Si_2H_4 = Si_2H_2 + H_2.$$

For plasma deposition as well as HWCVD deposition SiH_3 has been identified as the main precursor for deposition. In case of HWCVD, also some undesirable species originate near the filament. The highly reactive Si^* radicals, formed by the breaking of silane molecules at the catalyser surface generally get scavenged in the gas phase by reaction with silane molecules and the probability of Si^* radicals reaching the growing surface is substantially reduced by increasing either substrate to filament distance or process pressure. However, the species formed due to the scavenging reaction, i.e. Si_2H_4, would stabilize in the form of $Si_2H_2 + H_2$ species. The comparatively heavy Si_2H_2 radicals, having very small reactivity with SiH_4, can reach in substantial amount at the substrate if it is kept at ~3.5 cm (the typical distance that is often used in a HWCVD process) from the filament [11]. Our hypothesis is that these heavier species will have smaller diffusion length on the growing surface, especially at low substrate temperature and induce disorder in the film. The probability of any type of radical reaching the growing surface is a balance between its diffusion rate to the substrate and the

drift towards the pump. For a heavier species, because of a low diffusivity in the gas phase, the chance to be pumped away than to reach the substrate increases, if the distance to the substrate is increased. Thus, our hypothesis is that by increasing the substrate to filament distance, there is a higher probability that these heavier species can be pumped away, compared to SiH_3 radicals. The contribution of Si_2H_2 can be further reduced by increasing hydrogen dilution [11] and a material with very high structural order can be formed. This hypothesis explains the very low C-value observed for the HWCVD a-Si:H sample made at hydrogen to silane flow ratio of 20 and at a substrate to filament distance of 8 cm.

4. Conclusions

Amorphous silicon films with similar high photosensitivities can be made by both VHF PECVD as well as HWCVD with optimum hydrogen dilution of silane gas. However, the sensitivity of the structure to the deposition conditions differs significantly. At low hydrogen dilution conditions plasma CVD processes give better compact structure for a-Si:H, which again reinforces the beneficial effects of ion energy for amorphous materials. Significant improvement in density and structural order can be achieved for the HWCVD films made at low temperature by using hydrogen dilution. The presence of small (1–1.5 nm) dispersed crystalline-like islands in the silicon matrix and sharp rings in the selective area diffraction pattern point towards a special ordered structure. For a HWCVD deposited a-Si:H layer at 100 °C, a low structural disorder parameter of 1.67 and a small bond angle variation of 6.4° has been achieved. An increased filament to substrate distance is proposed as crucial parameter to improve the quality of low-temperature a-Si:H films by HWCVD.

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