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Intrinsic amorphous and microcrystalline silicon by hot-wire-deposition for thin film solar cell applications

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Abstract

The influence of various deposition parameters on the electrical and optical properties and the structure of amorphous and microcrystalline silicon films was investigated for material prepared by hot-wire (HW) CVD in a new multichamber deposition system, designed for the development of thin film solar cells. Prior to the material studies, careful measurement of the real substrate temperature under the influence of additional HW heating was performed. While good electronic quality and solar cell performance was found for a-Si:H layers, the μ c-Si:H material showed very high spin densities, porosity and a characteristic structural inhomogeneity along the growth axis. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the perspective of a considerable increase in conversion efficiencies, the use of microcrystalline silicon (μ c-Si:H) absorber layers in combination with amorphous silicon (a-Si:H) has been suggested, and much progress regarding the preparation and performance of µc-Si:H material and solar cells has been made [1-6]. For industrial production of solar cells, preparation of µc-Si:H offers an even higher challenge compared to the preparation of a-Si:H concerning development of high deposition rate processes and scaling-up to large areas. µc-Si:H prepared by plasma enhanced chemical vapor deposition (PECVD) at RF and VHF frequencies already shows excellent quality and performance in solar cells. Deposition rates were considerably improved compared to results obtained a few years ago, and the first successful scaling-up of PECVD processes for µc-Si:H were achieved [6-8]. However, the deposition rates are still too low for commercial production. On the other hand, much higher

deposition rates were reported for the preparation of μ c-Si:H with hot wire (HW) or catalytic (CAT) chemical vapor deposition (CVD) [9–11], a technique which also could have the potential of an easy up-scaling. However, the quality of the μ c-Si:H material prepared with HW-CVD and the performance of corresponding solar cells so far is much inferior compared to material and solar cells prepared with PECVD [10].

We, therefore, turned our attention to this alternative deposition technique for the preparation of μ c-Si:H in order to compare the potential of the deposition process and the resulting material to the already highly developed PECVD μ c-Si:H in our laboratory. A new multichamber deposition system, with three PECVD chambers for our standard μ c-Si:H solar cell process [4,5] and one HW-CVD chamber, was designed to incorporate HW-CVD absorber layers in working solar cell structures prepared by PECVD.

In the present paper we report the first results obtained using this new deposition system. Amorphous and microcrystalline silicon was prepared from silane/ hydrogen mixtures with a focus on the transition from amorphous to microcrystalline growth. In addition solar cells containing HW-CVD material, both amorphous and microcrystalline, were tested. Special attention was

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Fig. 1. Substrate temperature T_s as a function of heater temperature T_H for different filament temperatures T_t , and additional process gases.

devoted to the characterization of the HW-CVD system, in particular the substrate temperature T_s under various deposition conditions and the homogeneity of the deposition process over an extended substrate area.

2. Experiment

The films investigated in this paper were prepared in a multichamber deposition system with three PECVD chambers and one HW-CVD chamber. All chambers have a radiative substrate heater (diameter = 19 cm) 45 mm behind the substrate carrier. The HW set-up can hold several filaments at an adjustable distance between 40 and 100 mm from the substrate. The homogeneity of the films and the deposition rate can be improved by using more filaments in parallel. Films were prepared on borosilicate glass, quartz and crystalline silicon. For the hot wire we have used four tantalum [12] filaments with 0.5 mm diameter and a length of 18 cm at a typical distance of 7 cm from the substrate. In this configuration, deposition rates of 6 Å s⁻¹ for μ c-Si:H and more than 10 Å s⁻¹ for a-Si:H were achieved with a homogeneity better than $\pm 10\%$ on a substrate size of 10×10 cm².

The substrate temperature measurements were performed with three small PT-100 thermo-resistors (size $2 \times 2.3 \text{ mm}^2$) fixed to a glass substrate. A pyrometer was used to measure the filament temperature T_f . The samples were characterized by Raman and infrared (FTIR) spectroscopy, photothermal deflection spectroscopy (PDS), electron spin resonance (ESR) and dark conductivity and photoconductivity under AM 1.5 illumination.

The films had a thickness of 1.2–1.4 μ m and were, if not marked otherwise, prepared at a deposition pressure of $p_d=5$ Pa, a heater temperature of $T_H=400^{\circ}$ C and a filament temperature of $T_f=1650^{\circ}$ C ($P_{el}=700$ W), resulting in a substrate temperature of approximately 450°C.

The solar cells were deposited in the p–i–n sequence for the amorphous cells, using standard PECVD processes for the doped layers, and in an n–i–p sequence for the microcrystalline cells [4,5].

3. Results

3.1. Substrate temperature

Fig. 1 shows the substrate temperature T_s as a function of the heater temperature $T_{\rm H}$ with the filaments switched off, and for different filament temperatures $T_{\rm f}$ under vacuum and with different gases. Without filament heating, there is an almost linear relation between $T_{\rm H}$ and $T_{\rm S}$ with a good temperature homogeneity across the substrate (less than 30°C colder towards the edge). With the filaments switched on, there is a strong additional substrate heating such that at low $T_{\rm H}$ the substrate temperature is determined by $T_{\rm f}$, yielding $T_{\rm S} = 170^{\circ} \rm C$ for the conditions used here. The homogeneity improves with filament heating to only 10°C difference between center and edge of the substrate. Adding process gases (SiH_4, H_2) at a given filament temperature leads to a further increase of $T_{\rm S}$ while argon only causes little change in $T_{\rm S}$. Upon addition of SiH₄ or H₂, the filament heater power has to be increased to keep $T_{\rm f}$ constant. The thermo-resistors are not affected by the process gases or deposition due to their encapsulation.

This influence of process gases on T_s is also seen in the evolution of T_s , with additional filament heating under various conditions shown in Fig. 2. After a change of the parameters, such as filament heating or switching process gases, it takes approximately 30 min until the new equilibrium temperature at the substrate is reached.



Fig. 2. Evolution of substrate temperature $T_{\rm S}$ under various deposition conditions for $T_{\rm H}$ = 300°C.



Fig. 3. Dark- and photoconductivities for different sets of samples as a function of the silane concentration during deposition.

The reasons for this strong influence of the process gas on T_s and the different behaviors for different gases can only be speculated upon at this point. Possible effects include heat transport, energy losses through chemical reactions at the HW and changes of the HW surface by deposition of material.

3.2. Film characterization

3.2.1. Conductivity measurements

In Fig. 3, dark (σ_D) and photoconductivities (σ_{Ph}) are shown for material prepared with different silane concentrations (SC) and substrate temperatures. The sharp drop in σ_D indicates the transition between μc -Si:H at low SC and a-Si:H at high SC. This transition depends strongly on other deposition parameters like T_S or p_d (not shown). In contrast to the behavior of σ_D , σ_{Ph} remains remarkably unaffected by this transition.

3.2.2. Raman spectroscopy

In Fig. 4, Raman spectra are shown for samples prepared with different SC at 450° C (same samples as shown in Fig. 3). The spectra are taken with two different excitation wavelengths: at 488 nm contributions from the surface part of the film are emphasized, while at 647 nm homogeneous excitations across the 1-µm-thick sample can be assumed.

The 488-nm spectra show little difference in the film structure (ratio of intensity at 480 and 520 cm⁻¹) between SC=10 and 22% but a prominent contribution from amorphous phase at SC=25%. However, with 647-nm excitation a strong amorphous contribution is



Fig. 4. Raman spectra (taken at two excitation wavelengths) of HW samples prepared with different silane concentrations (T_s = 450°C).

still seen for the SC=19 and 22% samples. This suggests a structural inhomogeneity along the growth axis with considerable amorphous regions at the interface. These conclusions are supported by Raman spectra with excitation through the substrate (not shown), where already the samples prepared with SC=10% show a broad peak at 480 cm⁻¹. Only the sample prepared with SC=5% showed no sign of amorphicity.

3.2.3. FTIR spectroscopy

The IR spectra for the same sample series are shown in Fig. 5. We identify the well-known absorption modes for Si–H at $630/640 \text{ cm}^{-1}$, $850/890 \text{ cm}^{-1}$, $2000/2100 \text{ cm}^{-1}$, and strong absorption bands at $1000-1200 \text{ cm}^{-1}$ due to Si–O. For material prepared with SC=5– 22%, the characteristic Si–H stretching doublet at 2100



Fig. 5. Infrared absorption of HW-films grown with different silane concentrations measured by FTIR ($T_s = 450^{\circ}$ C).



Fig. 6. Spin densities for different silane concentrations, pressures and temperatures.

cm⁻¹ (Si–H at $\langle 111 \rangle$ and $\langle 110 \rangle$ surfaces [10,13,14]) is seen and the wagging mode is at 630 cm^{-1} . With increasing SC, the stretching mode at 2000 cm^{-1} develops at the cost of the doublet at 2100 cm⁻¹, indicating increasing amorphous contributions. At SC=25% the wagging mode is shifted to 640 cm⁻¹ and the Si-H surface doublet has disappeared. The Si-O absorption, which we consider an indication for porosity of the films, is particularly strong in material with high µc content. Using the evaluation method developed for a-Si:H we have estimated the hydrogen content $c_{\rm H}$ from the intensity of the absorption line at 630/640 cm⁻¹ [15,16]. For films prepared at $T_s = 450^{\circ}C$ (280°C) with SC = 5-22% we find $c_H = 0.8-1.5$ at.% (4 at.%) and $c_{\rm H}=3$ at.% at SC=25%. Note that this method can only determine the amount of bonded hydrogen. There are, however, indications for a considerable amount of molecular hydrogen in µc-Si:H [15,17].

3.2.4. Electron spin resonance

All microcrystalline HW films show a very high spin density $N_{\rm S}$ at a g-value of approximately 2.005 (Si dangling bond), which reaches a maximum value of 5×10^{18} cm⁻³ at $T_{\rm S}$ =450°C and SC=5%. $N_{\rm S}$ decreases with increasing SC, i.e. towards amorphous growth conditions and can be further reduced to a few times 10^{17} cm⁻³ at lower $T_{\rm S}$ and low deposition pressure (as shown in Fig. 6). Still, these values are an order of magnitude above the spin densities obtained for μ c-Si:H prepared with PECVD [18]. For purely amorphous material, the spin density is probably well below 10^{17} cm⁻³ (detection limit for the present experimental setup: sample size 4×13 mm², 1 μ m thickness, room temperature). The good quality of the HW a-Si:H material is confirmed by the solar cell performance described below.

3.2.5. PDS

Indications for such high defect densities in the HW-CVD μ c-Si:H material are also seen in the optical absorption spectra (Fig. 7). The spectra are distinctly different from spectra of μ c-Si:H prepared with PECVD, showing excess absorption over the entire energy range investigated. But surprisingly, no correlation between the strong variation of N_s with SC (Figs. 6 and 7) and the height of the sub-gap absorption can be found. Many samples exhibit a fringe pattern indicating an inhomogeneous absorption in the growth direction.

3.3. Solar cells with HW-i-layer

Absorption layers prepared by HW-CVD have been implemented into several solar cells, but have not been optimized so far. For amorphous cells we reached a maximum efficiency $\eta = 7.6\%$ [fill factor (FF) of 69.7%, open circuit voltage $V_{\rm oc} = 845$ mV, short circuit current density $I_{\rm sc} = 12.9$ mA cm⁻²] on an Asahi-U substrate. These values attest the high quality of the a-Si:H made by HW-CVD. The μ c-Si:H cells made with a HW-i-layer have a maximum efficiency $\eta = 2.6\%$ (FF = 51.6%, $V_{\rm oc} = 348$ mV, $I_{\rm sc} = 14.2$ mA cm⁻²) on a ZnO/Ag substrate for an i-layer close to the μ c/ amorphous transition at medium substrate temperatures ($T_{\rm H} = 300^{\circ}$ C, SC = 6%). The low efficiency is consistent with the high defect density observed in the absorber.



Fig. 7. Absorption of HW-films measured by PDS. The dotted line shows a high quality VHF-PECVD μ c-Si:H film for comparison ($T_{\rm S}$ = 450°C).

4. Summary

In our new multichamber deposition system both a-Si:H and μ c-Si:H films are grown at a deposition rate of up to 10 Å s⁻¹, with a homogeneity better than $\pm 10\%$ at a substrate size of 10×10 cm².

The influence of the HW filaments on the substrate temperature is rather high, with an additional heating by up to 200°C for some deposition conditions, but a good homogeneity across the substrate ($\pm 10^{\circ}$ C). Long time constants of approximately 20 min have been found despite the small thermal mass of the substrate carrier.

We have obtained high quality a-Si:H as judged by the material properties as well as by the solar cell performance, but the µc-Si:H is still of poor quality. In contrast to our experience with µc-Si:H from PECVD processes [18] and results from other groups [19], we observe a higher DB density for increasing crystallinity. The sub-gap absorption remains surprisingly unaffected by these changes in the DB density. At $T_s = 450^{\circ}$ C the μc-Si:H films show a strong structural inhomogeneity along the growth axis. Only the sample with the lowest SC (=5%) exhibits a complete absence of the amorphous phase, but this sample also has the highest DB density and the strongest Si-O absorption in IR spectroscopy. At higher SC an amorphous contribution is visible in IR and Raman and is continuously growing, until the samples are amorphous at an SC = 31%.

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