Structure adjustment during high-deposition-rate growth of microcrystalline silicon solar cells

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Preparation of microcrystalline silicon for solar cell applications is investigated under high-pressure, high-power conditions with plasma-enhanced chemical vapor deposition at 95 MHz. It is found that the deposition rate depends mainly on the amount of silane in the reaction zone. Changes in the discharge power affect the deposition rate very little. This points to silane depletion under these process conditions. The amount of H radicals, on the other hand, increases with increasing discharge power and leads to structure changes of the material. Making use of this effect, optimum phase mixture material at the transition from highly crystalline to amorphous growth can be deposited at considerably higher deposition rates without loss in solar cell performance. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1801676]

The preparation of microcrystalline silicon (μc-Si:H) with plasma enhanced chemical vapor deposition processes has made considerable progress over the last ten years in view of deposition rates for high quality material for solar cell applications. A breakthrough was the use of higher plasma excitation frequencies in plasma enhanced chemical vapor deposition (PECVD) in place of the standard 13.56 MHz.[1–3] Further decisive contributions were made when turning back to the 13.56 MHz excitation by use of the high-pressure, high-power (hphP) method,[4–6] and finally by combination of high excitation frequencies (VHF) with hphP.[5,7–11]

In using both VHF and hphP for deposition of μc-Si:H a main idea is to reduce the maximum energy of ions impinging on the substrate while applying high excitation power to obtain an effective gas dissociation and a high ratio of hydrogen over SiH$_x$ ($x<4$) radicals. This is achieved with high excitation frequencies where sheath voltages are reduced and with high pressure where a reduced mean free path leads to ion energy loss by collision.

High ion energies are considered to be detrimental for μc-Si:H growth.[12] On the other hand it has been proposed that a high ion flux in VHF-PECVD is beneficial for high growth rates via ion-induced desorption of hydrogen from the growth surface.[13] Optimization of ion flux versus ion energy might therefore be of importance for high growth rate processes.

In any case a high ratio of atomic H over SiH$_x$ ($x<4$) radicals is considered a main prerequisite for μc-Si:H growth (see Ref. 11 for a recent study in the VHF-hphP regime). We will not elaborate on the details of the plasma processes and the growth mechanism for μc-Si:H formation,

which has been the subject of numerous studies in the past. A good review of the present understanding and literature is given in Ref. 14. However, the concept of silane depletion, which has been suggested to be particularly important for growth of μc-Si:H under high pressure,[5] shall be of interest here. It says that the reaction

$$SiH_4 + H \rightarrow SiH_3 + H_2, \tag{1}$$

where silane annihilates atomic hydrogen, has to be prevented in order to maintain a high H/SiH$_x$ ($x<4$) ratio, particularly under high pressure condition. Reaction (1) is unlikely if the silane molecule density is kept at a low enough level by strong hydrogen dilution or by high discharge power where large amounts of silane are decomposed in initial reactions of type SiH$_4 \rightarrow$ SiH$_x+(4-x)$H. If most of the silane molecules are decomposed into growth precursors, one would, to a first approximation, observe no increase of the deposition rate with an increase in discharge power. But the increase in discharge power would increase the H/SiH$_x$ ($x<4$) ratio further. This should influence the growth conditions of μc-Si:H resulting in different crystalline-to-amorphous volume fractions, different grain sizes, possibly differences in other microstructure features such as columnar growth and porosity, and finally possible differences in the defect densities. For this reason, an adjustment of the μc-Si:H structure formation is vital for the optimization of the solar cell performance if the deposition power or pressure is changed, because it has been found that the highest solar cell efficiencies with μc-Si:H absorber layers are obtained at growth conditions near the transition from fully crystalline to amorphous growth.[6,8,15–17] It is argued that optimum material benefits from surface passivation by residual amorphous phase, which also makes the material more compact and less susceptible to indiffusion of atmospheric gases after deposition.[17,18]

We report on the effect of the discharge power under VHF-hphP conditions on the structure formation of μc-

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Si:H and the consequences for the performance of the material in solar cells. The silane concentration SC $=[SiH_4]/([SiH_4]+[H_2])$, defined by the gas flow ratio of silane and hydrogen, was varied for each deposition power, covering the entire structural composition regime from highly crystalline to amorphous. We have adopted the VHF-hphP process as described in the literature[5,7,9,10] and have adjusted the process to our cluster tool deposition system.[16] The electrode configuration consists of a 13.5-cm-diam powered electrode and a 12×12 cm^2 substrate carrier in a carrier support as the grounded electrode. Substrate size is 10×10 cm^2. The electrode distance is easily variable *in situ* between 60 and 12 mm. An electrode distance of 12 mm was used unless otherwise stated. A metal shield around the electrodes to prevent deposition on the chamber walls can be removed for discharge adjustment. The gas supply is a simple cross-flow geometry, i.e., no gas showerhead arrangement.

Substrate temperatures were about 200°C for *p*-, *i*-, and *n*-layer deposition. The μc-Si:H *p*-layers were deposited with VHF-PECVD at 95 MHz and 0.25 hPa. The *a*-Si:H *n*-layers were deposited at 13.56 MHz. The μc-Si:H *i*-layers were deposited with the VHF-hphP method at 95 MHz. The VHF input power was varied between 20 and 60 W. The total pressure was 2 or 4 hPa.

Solar cell structure is glass/Ag grid/textured ZnO/*p-i-n*/Ag. The 1×1 cm^2 backcontact defines the individual solar cell area. Deposition times for the *i* layers were adjusted to obtain approximately 1-μm-thick absorber layer in all cases. The thickness of the solar cells was measured with a step profiler neglecting the thickness of the doped layers (total of about 50 nm). The deposition rate was calculated from the thickness measurement in the middle of the substrate. The thickness variation between middle and edge of the substrate was typically about 10%. The *I/V* diode characteristics of the solar cells are measured with AM1.5 illumination at 25°C.

Raman scattering measurements with the 488 nm line of an argon laser for excitation were performed on the solar cells after removal of the amorphous *n* layer in between the Ag backcontact areas. The ratio of the integrated intensities (I_C^{RS}) of the Gaussian peaks fitted to Raman signal, attributed to crystalline grains (at 500 and 520 cm^{-1}) and disordered regions (480 cm^{-1}), $I_C^{RS}=(I_{500}+I_{520})/(I_{480}+I_{500}+I_{520})$ are used as a semiquantitative value of the crystalline volume fractions.[19]

Figure 1 shows R_D measured on solar cells versus silane concentration for discharge power between 20 and 60 W at total flow of 100 sccm and pressure of 2 hPa. Additionally, data for deposition series with 60 W and 4 hPa, an increased electrode distance of 19 nm, or a total flow of 200 sccm are shown. All depositions were performed with plasma shield except one series at 2 hPa/60 W at a later stage, where the shield was removed. Removal of the metallic shield resulted in less parasitic losses of discharge between electrode and shield, thus requiring a considerably lower minimum power to sustain a stable plasma. As a consequence less powder was accumulated at the electrode edges, which in turn led to better stability of the individual discharge as well as from run to run. It was found that at high working pressure, the removal of the shield has no big effect on the R_D and the plasma is well confined in between the electrodes. Depositions without shield shall therefore be used in any future deposition. For
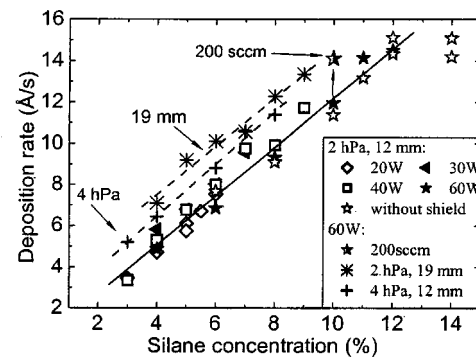

FIG. 1. Deposition rates of solar cells where the *i* layers were prepared in the VHF-hphP regime with different power, pressure, gas flow, and electrode distance plotted against silane concentration. If not indicated otherwise, a pressure of 2 hPa, an electrode distance of $d=12$ mm, and a total flow rate of 100 sccm were used. Samples deposited without plasma shield at 60 W are shown by open stars.

the 2 hPa/100 sccm condition the deposition rate depends very little on the discharge power between 20 and 60 W, while the deposition rate R_D increases linearly with SC. These observations suggest silane depletion under such conditions. A further increase in power hardly increases the silane radical production and the deposition rate is only determined by the amount of available silane. Consequently, as shown in Fig. 1, R_D increases by (i) increasing the pressure to 4 hPa, (ii) increasing the total flow to 200 sccm, doubling [SiH$_4$] and [H$_2$], or (iii) increasing the electrode distance. A higher deposition pressure enhances the residence time of the molecules in the deposition chamber. A higher electrode distance increases the ratio of the volume between the electrodes to that of the deposition chamber. In both cases silane molecules have a higher probability to diffuse into the reaction zone between the electrodes.

On the other hand, under silane depletion condition, when increasing the discharge power the number of H radicals should increase further. This change in H/SiH$_x$ ($x<4$) ratio affects the structure of the μc-Si:H *i* layer with important consequences for the growth conditions of optimum phase mixture material.

At an electrode distance of 19 mm, although good thickness homogeneity can be obtained, solar cells exhibit big structural difference between the center and the border of the 10×10 cm^2 substrate. By reducing the electrode distance to 12 mm, the homogeneity greatly improved and adequate solar cell performance uniformity can be obtained.

In Fig. 2 the solar cell *J-V* parameters efficiency η, open circuit voltage V_{OC}, fill factor FF, and short circuit current density J_{SC}, are plotted versus SC for the deposition with VHF-hphP at 2 hPa for various discharge power (same samples as in Fig. 1). Parameters are from the best 1 cm^2 cell of each 10×10 cm^2 sample. Typical relative efficiency variations across the substrate are within 5%. For each discharge power we observe the typical behavior for μc-Si:H solar cells when varying the structure from highly crystalline to amorphous by variation of the SC.[6,8,15–17] Starting at low SC values, η, FF, and J_{SC} increase with SC, reach a maximum, and decrease at the highest SC while the V_{OC} increases over the entire SC range. This behavior indicates a structure change from highly crystalline to amorphous in the absorber material, which is confirmed by Raman data as specified in the figure for selected samples. Note that for the series with-
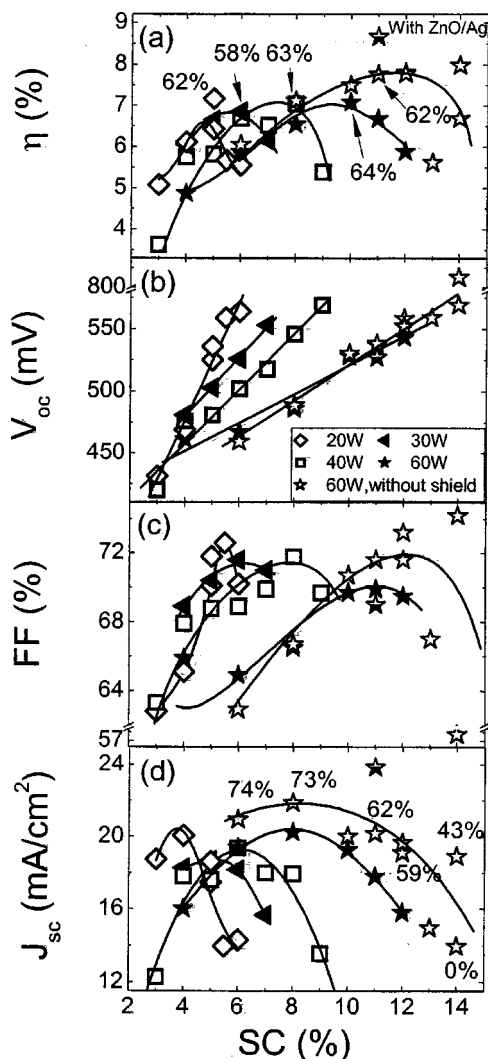
FIG. 2. AM1.5 illuminated $J-V$ characteristics of solar cells deposited with different plasma powers. Solar cells, the same samples as in Fig. 1, are ~ 1 μm thick and 1×1 cm^2 large, defined by simple Ag backcontacts. A thicker solar cell with highly reflective ZnO/Ag backcontact is also shown by the half star. I_C^{RS} values of optimum cells are indicated in (a). The structure evolution with SC in terms of I_C^{RS} shown for selected samples in (d). Lines are guides for the eyes.

out shield an improved p-layer results in overall higher J_{SC} values. The most important observation however is the shift to higher SC of the maximum values in η, FF, and J_{SC} upon the increase of the discharge power. This supports the assumption that although the increase in power does not further increase SiH$_x$ radical production, and therefore does not increase the deposition rate, a higher power increases the H/SiH$_x$ ratio, which results in different growth conditions. The μc-Si:H to a-Si:H transition is shifted to higher SC for higher discharge powers, as indicated by the I_C^{RS} values. Consequently the conditions for optimum solar cell performance, which are found near the crystalline to amorphous transition,[15–17] are also shifted to higher SC and therefore to higher R_D. The maximum efficiencies are similar for each discharge power. Note that all solar cells have an absorber layer thickness of 1 μm and a simple Ag metal backreflector

only. Given these conditions, the J_{SC} values are very high in these solar cells. Together with the high fill factors this points to very good material quality of the VHF-hphP material.

As a consequence of the shift of the optimum phase mixture to higher silane concentrations with an increase in the discharge power, the deposition rate for such material increases considerably when using higher power (compare Fig. 1). A μc-Si:H pin diode was prepared at 2 hPa/60 W at SC=11% with 14.6 Å/s. With an absorber layer thickness of 1.6 μm and a highly reflective ZnO/Ag backcontact it shows an efficiency of 8.7 %, indicated in Fig. 2 by half star.

In summary: When working in the high pressure high power deposition regime at VHF, deposition conditions for optimum phase mixture μc-Si:H material for solar cell applications have to be adjusted by variation of silane concentration and discharge power. The increase of the deposition power yields hydrogen radical concentrations above the optimum level for μc-Si:H solar cell material which can be compensated by an increase of the silane concentration. Thereby, deposition rates for high quality μc-Si:H absorber layers can be increased to values around 15 Å/s.

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