Microcrystalline silicon solar cells deposited at high rates

Y. Mai, S. Klein, R. Carius, J. Wolff, A. Lambertz, and F. Finger
Institut für Photovoltaik (IPV), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

X. Geng
Institute of Photoelectronics, Nankai University, Tianjin 300071, People’s Republic of China

(Received 21 January 2005; accepted 6 April 2005; published online 3 June 2005)

Hydrogenated microcrystalline silicon (μc-Si:H) thin-film solar cells were prepared at high rates by very high frequency plasma-enhanced chemical vapor deposition under high working pressure. The influence of deposition parameters on the deposition rate (R_d) and the solar cell performance were comprehensively studied in this paper, as well as the structural, optical, and electrical properties of the resulting solar cells. Reactor-geometry adjustment was done to achieve a stable and homogeneous discharge under high pressure. Optimum solar cells are always found close to the transition from microcrystalline to amorphous growth, with a crystallinity of about 60%. At constant silane concentration, an increase in the discharge power did hardly increase the deposition rate, but did increase the crystallinity of the solar cells. This results in a shift of the μc-Si:H/a-Si:H transition to higher silane concentration, and therefore leads to a higher R_d for the optimum cells. On the other hand, an increase in the total flow rate at constant silane concentration did lead to a higher R_d, but lower crystallinity. With this shift of the μc-Si:H/a-Si:H transition at higher flow rates, the R_d for the optimum cells decreased. A remarkable structure development along the growth axis was found in the solar cells deposited at high rates by a “depth profile” method, but this does not cause a deterioration of the solar cell performance apart from a poorer blue-light response. As a result, a μc-Si:H single-junction p-i-n solar cell with a high efficiency of 9.8% was deposited at a R_d of 1.1 nm/s. © 2005 American Institute of Physics. [DOI: 10.1063/1.1927689]

I. INTRODUCTION

High growth rate of microcrystalline silicon (μc-Si:H) with plasma-enhanced chemical vapor deposition (PECVD) requires reasonably high discharge power for high dissociation of the reactant gases, leading to higher sheath voltages, and thus higher ion energy. High-energy ions impinging on the growth surface, however, are considered to be detrimental to the quality of μc-Si:H, causing defect formation and deterioration in crystallinity.1,2 Therefore, suppressing the high-energy ions in the plasma is of particular necessity at a high discharge rate (R_d). A way to reduce ion energies in PECVD systems is the use of a third electrode in a triode arrangement.1,3,4 With an independent bias on this electrode with respect to the grounded substrate, ion energies can be controllably reduced. Other effective methods to reduce ion energies while maintaining high deposition rates are (i) very high frequency (VHF) excitation of the discharge, where lower peak-to-peak voltages for a given discharge power result in lower maximum-ion energies,5–9 and (ii) high working pressure (p_depo) with an increased discharge power, where ion energies are reduced by multiple collisions in the plasma sheath.10–12 Recently, also combinations of VHF-PECVD and high working pressure have been investigated.3,13–17 In the present paper we report on further studies of such a combination of VHF-PECVD at 94.7 MHz at high working pressures of 2–4 hPa for the growth of μc-Si:H at high deposition rates. As high pressure is combined with high discharge power, we shall refer to this deposition regime as high pressure–high power (hphP) in contrast to the low power–low pressure (lplP) conditions in conventional RF- and VHF-PECVD.

While the reduction of the ion energies by a combination of high excitation frequency and high working pressure is successfully reducing the damage on the growing surface, such energy loss and unwanted leak discharges can, on the other hand, result in disruption of the glow discharge. Therefore, a discharge reactor geometry adjustment, different from the optimum settings in RF- or VHF-PECVD at low p_depo (typically 0.3 hPa), is generally necessary at high p_depo. This will first be discussed in this report. After having defined a reactor geometry for a stable and homogeneous discharge, deposition of μc-Si:H absorber layers in p-i-n solar cells are carried out with variations of the discharge power P_vhf, the working pressure p_depo, and the total gas flow rate F_l total. For each set of deposition condition, the silane concentration (SC) is varied so as to cover the entire range of material growth from highly crystalline to amorphous, in order to find the optimum phase mixture (OPM) material. Such OPM material, which results in the highest solar cell efficiencies, was found close to the transition from highly crystalline to amorphous growth in several earlier studies with different deposition methods.12,18,19 Here we show that a similar behavior is found for the VHF-PECVD under high working pressure and high power (hphP) conditions. The shift of the OPM growth regime upon the variation of the deposition conditions, such as power and gas flow, and the behavior of the...
growth rates shall be discussed with an illustrative scheme for μc-Si:H growth, with the ratio of H over SiH₂ (x = 1, 2, or 3, same hereinafter) radicals as the key parameter.

On the other hand, the solar cell performance is related to the $i$-layer material properties. For this purpose, in addition to current–voltage ($J–V$) measurements on the solar cells under illumination, measurements of the quantum efficiency (QE) and of the dark $J–V$ are performed. Points of concern when using high-deposition-rate methods are that material growth might be affected by the insufficient relaxation of growth precursors and the development of a pronounced disordered interface between the $p$ and the $i$ layers in the case of a $p$-$i$-$n$ junction. This would affect the solar cell performance through reduced carrier collection and would show as a reduced blue-light response. Therefore, we have investigated, in particular, the structure composition of the absorber-layer material and the development of the structure along the growth axis with Raman spectroscopy. For the latter a powerful “depth profile” method, including crater etching and Raman-scattering measurements with different excitation wavelengths, is introduced.

II. EXPERIMENTAL DETAILS

The $p$, $i$, and $n$ layers of the μc-Si:H solar cells were deposited in individual chambers of a cluster-tool deposition system by PECVD to form $p$-$i$-$n$ single-junction diodes. Figure 1 shows a schematic picture of the deposition chamber. The electrode configuration consists of a 13.5-cm-diameter powered electrode and a $12 \times 12$-cm² substrate carrier in a carrier support as the grounded electrode. Substrate size is $10 \times 10$ cm². The electrode distance is easily variable in situ between 60 and 12 mm. A metal shield around the electrodes to prevent deposition on the chamber walls, as indicated in Fig. 1, can be removed for discharge adjustment. The gas supply is a simple cross-flow geometry, i.e., no gas showerhead arrangement.

Solar cells are deposited on texture-etched ZnO-coated glass substrates. Substrate temperatures are $\sim 200$ °C for $p$-, $i$-, and $n$-layer depositions. The μc-Si:H $p$ and $i$ layers were deposited with VHF-PECVD at 94.7 MHz. The $a$-Si:H $n$ layers were deposited with conventional RF-PECVD at 13.56 MHz. The silane concentration, $SC = [SiH_4]/([SiH_4] + [H_2])$, defined by the gas-flow ratio of silane and hydrogen was varied in each case to adjust the structure mixture of the $i$-layer material from highly crystalline to amorphous.

The area of individual solar cells is defined by the $1 \times 1$-cm² evaporated Ag back contact. The deposition time for the $i$ layers was adjusted to obtain a thickness of approximately $1 \mu$m. The thickness of the solar cells was measured with a step profiler (Dektak 3030, VEECO Instruments GmbH), neglecting the thickness of the doped layers (total of about 50 nm). The deposition rate was calculated from the thickness measurement in the center of the substrate. The thickness variation between the center and the edge of the substrate was typically about 10%. The $J–V$ characteristics of the solar cells, i.e., efficiency $\eta$, open-circuit voltage $V_{OC}$, fill factor FF, and short-circuit current density $J_{SC}$, were measured under AM1.5 illumination at 25 °C after a 30-min annealing in air at 160 °C. The $J–V$ curves measured in the dark are used to obtain information about the recombination behavior in the solar-cell absorber layers. Quantitative spectra are used for information about the optical absorption and the charge-carrier extraction.

Raman-scattering measurements performed on the solar cells, after the removal of the amorphous $n$ layers by KOH etching, provide direct information about the relationship between the structural properties and solar cell performance. The 488-nm line of an argon laser is usually used for excitation, and more than 50% of the Raman signal at this wavelength was contributed from the topmost 200 nm of the $i$ layer. In order to find out the structure evolution in the growth direction, a depth-profile method is introduced here. Craters with different depths created by KOH etching make it possible to obtain the structure information at different stages of growth directly by Raman-scattering measurement. Choosing the appropriate KOH solution concentration, etching temperature, and etching time, different crater depths with sufficient smoothness at the bottom can be achieved, which can be monitored by the step profiler. Figure 2 shows an exemplary picture of a crater measured by the step profiler. The 4-mm-long and 2-mm-wide flat bottom allows an accurate Raman measurement with the $2 \times 0.3$-mm² large laser spot. Raman-scattering measurement with a longer excitation wavelength of 647 nm, with most of the signal contributed from the topmost 1 μm of the $i$ layer in the solar cells, here the whole $i$ layer, is used as an easy and supplementary method to the crater etching. The ratio of the integrated intensities of Gaussian peaks fitted to the Raman signal attributed to crystalline grains (at 500 and 520 cm⁻¹) and disordered regions (480 cm⁻¹), $I_{c\text{RS}} = (I_{500} + I_{520})/(I_{480} + I_{500} + I_{520})$, is used as a semiquantitative value of the crystalline
volume fraction. We use $I_{C}^{RS}$ and $I_{C}^{RS}$ to specify the $I_{C}^{RS}$ values calculated from Raman spectra with 488 and 647-nm excitation, respectively.

### III. RESULTS

#### A. High-rate deposition under hphP condition

In the first part, investigations of the influence of the deposition parameters, such as $P_{dep}$, $P_{VHF}$, $F_{total}$, and electrode distance $d$, on the discharge stability, the deposition rate $R_{p}$, and the solar cell properties will be presented. For the individual deposition conditions, variations of the silane concentration SC were performed to cover the range from highly crystalline to amorphous growth and to obtain the optimum solar cells. For a detailed information on the deposition parameters in each SC series, see Table I. The first column shows the names assigned to the SC series, which will be used hereafter for the presentation and discussion of the results. Data for one series of solar cells deposited under low-pressure, low-power (lplP) conditions at $R_{p}$ between 0.12 and 0.35 nm/s are also presented for comparison. $R_{p}$ and the conversion efficiency for the optimum solar cell in the lplP series are about 0.2 nm/s and 8%, respectively. The results for this lplP series are in excellent agreement with earlier work, and the solar cell parameters show the well-known behavior as a function of SC, i.e., the variation of the crystalline volume fraction.

In the hphP series with different $F_{total}$ and in the lplP series, an improved, thinner $p$ layer, yielding higher blue-light response, is used. In the $i$-layer deposition of these solar cell, the metallic shield around the powered electrode was removed to obtain more stable deposition conditions. This will be discussed in the following section.

#### 1. Stable and homogeneous deposition under high $P_{dep}$

Deposition processes in the hphP regime promise a considerable increase in the growth rate, but the low electron energy, caused by a reduced mean free path under high-pressure conditions and by a low peak-to-peak voltage at high plasma-excitation frequency, make it difficult to start and sustain stable discharges. For this reason, an adequately high discharge power and/or a small electrode distance are necessary for the combination of VHF and high pressure. Figure 3 shows the minimum power, which is required for a given $P_{dep}$ in order to maintain a stable plasma at different electrode distances ($d$). The necessary $P_{VHF}$ sharply increases with $P_{dep}$ at a constant electrode distance. At smaller distances, where a stronger electric field is available, lower $P_{VHF}$ is sufficient at a given $P_{dep}$. All combinations of $P_{VHF}$ and $P_{dep}$ yielding stable plasma conditions should be located above the corresponding line for a given electrode distance. Leading to high $R_{p}$ and simultaneously providing a wide deposition parameter space within the system’s technical limit, the pressure of 2.1 hPa is the one generally used under the hphP condition in this paper. The removal of the metallic shield resulted in less parasitic losses of the discharge between electrode and shield, requiring a considerably lower minimum power to sustain a stable plasma. As a consequence, also less powder was accumulated at the electrode edges, which in turn led to a better stability of the individual discharge as well as from run to run. Furthermore, it was observed that under high working pressure, the plasma was well confined in between the electrodes, with no plasma burning at other places after the removal of the shield. Therefore, depositions in the later stage of the present research work have been carried out without a shield. The comparison of the solar cell performance showed that the removal of the

---

**TABLE I. Deposition parameters of the silane concentration (SC) series.**

<table>
<thead>
<tr>
<th>Series name (SC)</th>
<th>$P_{dep}$ (hPa)</th>
<th>$P_{VHF}$ (W)</th>
<th>$F_{total}$ (SCCM)</th>
<th>$d$ (mm)</th>
<th>Shield</th>
<th>$p$ layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>hphP 20 W</td>
<td>2.1</td>
<td>20</td>
<td>100</td>
<td>12</td>
<td>with</td>
<td>Normal</td>
</tr>
<tr>
<td>hphP 30 W</td>
<td>2.1</td>
<td>30</td>
<td>100</td>
<td>12</td>
<td>with</td>
<td>Normal</td>
</tr>
<tr>
<td>hphP 40 W</td>
<td>2.1</td>
<td>40</td>
<td>100</td>
<td>12</td>
<td>with</td>
<td>Normal</td>
</tr>
<tr>
<td>hphP 60 W</td>
<td>2.1</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td>with</td>
<td>Normal</td>
</tr>
<tr>
<td>hphP 90 W</td>
<td>2.1</td>
<td>90</td>
<td>100</td>
<td>12</td>
<td>with</td>
<td>Normal</td>
</tr>
<tr>
<td>hphP 19 mm</td>
<td>2.1</td>
<td>60</td>
<td>100</td>
<td>19</td>
<td>with</td>
<td>Normal</td>
</tr>
<tr>
<td>hphP 4 hPa</td>
<td>4.0</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td>with</td>
<td>Normal</td>
</tr>
<tr>
<td>hphP 100 SCCM</td>
<td>2.1</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td>w/o</td>
<td>Improved</td>
</tr>
<tr>
<td>hphP 200 SCCM</td>
<td>2.1</td>
<td>60</td>
<td>200</td>
<td>12</td>
<td>w/o</td>
<td>Improved</td>
</tr>
<tr>
<td>hphP 400 SCCM</td>
<td>2.1</td>
<td>60</td>
<td>400</td>
<td>12</td>
<td>w/o</td>
<td>Improved</td>
</tr>
<tr>
<td>lplP</td>
<td>0.25</td>
<td>10</td>
<td>100</td>
<td>19</td>
<td>w/o</td>
<td>Improved</td>
</tr>
</tbody>
</table>

Note: 1 hPa= 1 mbar

---

**FIG. 3.** Minimum discharge powers to sustain a stable discharge as a function of $P_{dep}$ for different electrode distances.
shield has no major influence on the deposition rate or the solar cell properties, apart from the improved process stability.

In addition, the reduction of the electrode distance also improves the homogeneity of the discharge across the substrate. At an electrode distance of 19 mm, which is the electrode distance $d$ used for VHF-PECVD in the lplP series, already a considerable increase of $R_D$ could be achieved by applying high pressure and high $P_{\text{VHF}}$ (e.g., 1.23 nm/s, optimum cell in hphP 19-mm series), compared to the typical $R_D$ ($\sim$0.2 nm/s) under lplP conditions. However, such samples suffer from strong structural inhomogeneities on a substrate size of $10 \times 10$ cm$^2$. By reducing the electrode distance to 12 mm, the homogeneity greatly improved. Relative efficiency variations across the substrate are typically about 10%, except for some solar cells in the corners of substrates in some cases. Therefore, the majority of the investigations in this report were performed with an electrode distance of 12 mm and $p_{\text{depo}}$ of 2.1 hPa.

### 2. Effect of $P_{\text{VHF}}$ on the $R_D$ and solar cell performance

Five different discharge powers, $P_{\text{VHF}}$ of 20, 30, 40, 60, and 90 W, were applied to investigate the influence of discharge power on $R_D$ and on the properties of $\mu c$-Si:H solar cells at high deposition pressures. The input and reflected powers are nominal values measured by a directional power meter (Rhode & Schwartz NAP meter, power head: NZ-4) between the VHF generator and the matching network. To guarantee good power coupling into the discharge, care was taken by using large-diameter cables and a corresponding electric vacuum feed through, short cable lengths, and individually adjusted matching networks. The measured reflected power was typically below 1%. However, the “real” power dissipated in the discharge might be very different from the nominal input power. Details shall not be considered here. The $R_D$ of these SC series with different $P_{\text{VHF}}$ are shown in Fig. 4 as functions of SC. In addition, two series of solar cells were prepared with larger electrode distance (hphP 19 mm) or higher $p_{\text{depo}}$ (hphP 4 hPa) at $P_{\text{VHF}}$=60 W. The results for the deposition rates of these series are also plotted in Fig. 4. A linear increase of $R_D$ with increasing SC is observed in all cases. At $P_{\text{VHF}}$=90 W, the plasma became unstable and a considerable scatter of $R_D$ was observed. Further geometry rearrangement is necessary for such high $P_{\text{VHF}}$ for the present reactor design. The increase of $P_{\text{VHF}}$ does not result in any significant increase of $R_D$ at a fixed SC and above a certain $P_{\text{VHF}}$, $R_D$ even decreases. Assuming that up to 60 W the real power in the discharge at least increases to some extent, such a behavior indicates a depletion of the silane source gas. On the other hand, increasing $p_{\text{depo}}$ or the electrode distance $d$ at a given discharge power of 60 W results in higher $R_D$ for all SC compared with the other series deposited at 2.1 hPa and a 12-mm electrode distance.

Figure 5 shows the J–V characteristics for these series of solar cells deposited with different $P_{\text{VHF}}$ at 2.1 hPa. For each $P_{\text{VHF}}$ we observe a similar behavior of J–V parameters for $\mu c$-Si:H solar cells when varying SC, except the scattered results in the hphP 90-W series. FF and $J_{\text{SC}}$ first increase with SC and drop after reaching the maximum point. $V_{\text{OC}}$ increases almost linearly in the investigated SC range. The solar cells with maximum efficiency are obtained at a $V_{\text{OC}}$ of 540 mV. Note that the J–V parameters are taken from the best $1 \times 1$-cm$^2$ cell of each $10 \times 10$-cm$^2$ substrate. The low $J_{\text{SC}}$ at high SC is attributed to the red and infrared response loss in these solar cells. This is confirmed by using a cutoff filter during J–V characteristics measurement. The highest FF in each SC series decreases systematically upon the increasing $P_{\text{VHF}}$, but a significant drop of the optimum cell efficiency was only observed at $P_{\text{VHF}}$=90 W. The most im-
important observation is the shift of the maximum values in efficiency, FF, and $J_{SC}$ to higher SC upon the increase of the discharge power. As a consequence, optimum cells deposited with higher $P_{VHF}$ have higher $R_D$, as indicated in Fig. 6, in which efficiency, $R_D$, and the required SC of the optimum cells of these series are plotted versus $P_{VHF}$. The required SC for optimum solar cells increases linearly with $P_{VHF}$. The increase of the silane supply leads to a linear increase of $R_D$ below 60 W.

The optimum cells of the hphP 19-mm and hphP 4-hPa series show a lower conversion efficiency of about 6% and a strong structural inhomogeneity over the $10 \times 10$-cm$^2$ substrates.

3. Effect of $F_{total}$ on the $R_D$ and solar cell performance

As was shown in Fig. 4, an increase of the discharge power at hphP conditions from 20 to 60 W does not lead to an increase in the deposition rate at constant SC, while the deposition rate increases linearly with silane concentration, i.e., the source gas supply. This points to the silane depletion under these conditions. It means that at a given SC, the precursor density cannot be increased much by a higher discharge power. A possible solution to this problem would be to increase the reaction zone volume or to increase the silane supply by a higher gas flow. As an additional beneficial effect of a higher gas flow, powder formation, which is frequently observed in high-deposition-rate processes, could possibly be suppressed due to the resulting short gas residence time. Three different $F_{total}$, 100, 200, and 400 SCCM (standard cubic centimeter per minute), were used to prepare $\mu$-c-Si:H solar cells at a discharge power of 60 W and a pressure of 2.1 hPa. Again, SC series were done to cover the range from a highly crystalline to an amorphous material structure. Furthermore, the metallic steel shield around the powered electrode was removed in the $i$-layer deposition. Figure 7 shows the $R_D$ of the solar cells deposited at different flow rates, plotted against SC. A linear increase of $R_D$ with increasing SC is observed at each different $F_{total}$. At constant SC, doubling $F_{total}$ increases, but far from doubles, the $R_D$, resulting in lower gas utilization at higher $F_{total}$. The comparison with the hphP 60-W series, shown in Fig. 4, which was deposited with the metallic shield, shows that the removal of the shield makes no difference in the $R_D$.

The $J$–$V$ characteristics of these series of solar cells deposited at different $F_{total}$ are shown in Fig. 8. Similar dependencies of $\eta$, $V_{OC}$, $J_{SC}$, and FF with the variation of SC are observed for all different $F_{total}$. Compared with the hphP 60-W series in Fig. 5, thinner $\rho$ layers in the hphP 100-SCCM series increase the blue-light response and thus $J_{SC}$, leading to higher efficiencies. At constant SC, solar cells deposited with higher $F_{total}$ exhibit higher $V_{OC}$, suggesting a lower crystallinity in the $i$ layers. In Fig. 9, $R_D$, $\eta$, and SC of the optimum cells, deposited with different $F_{total}$ are shown. An increase in $F_{total}$ from 100 to 400 SCCM results in a
slight increase of the $\eta$ of the optimum cells. At higher $F_{\text{total}}$ the required SC for optimum solar cells is shifted to a lower SC, leading to a lower $R_D$ for the optimum cells and suggesting a corresponding shift of the $\mu$-Si:H/a-Si:H transition.

Applying the optimized material of the hphP 100-SCCM series at a SC of 11%, a thicker solar cell with 1.4-µm $i$-layer thickness was deposited at 1.2 nm/s. With the incorporation of the highly reflective ZnO/Ag back contact, it shows a conversion efficiency of 9.2% (Fig. 10). An increase of the total flow rate up to 400 SCCM decreases the $R_D$ of the optimum cell a little (~1.1 nm/s), but increase the efficiency. The 2.0-µm-thick optimum cell with ZnO/Ag back contact shows a very high efficiency of 9.8% (also in Fig. 10).

Due to the considerable longer gas residence times under hphP conditions, powder formation is more pronounced than with a conventional low working pressure. However, powder formation did not affect the reproducibility and homogeneity of the solar cell preparation. Typically high-performance solar cells could be prepared up to a total layer thickness of at least 20 µm in the reaction chamber before chamber cleaning was needed.

4. Solar cell performance versus $R_D$

Applying the VHF-PECVD in the lplP and hphP regime, respectively, $\mu$-Si:H solar cells can be deposited over a wide range of $R_D$ between 0.2 and 1.5 nm/s without a detrimental influence of the high deposition rate on the solar cell performance.

In Fig. 11, $V_{\text{OC}}$ and FF of $\mu$-Si:H solar cells with high conversion efficiencies are plotted against their $R_D$ and the deposition regime. $J_{\text{SC}}$ is not taken into account here because it is easily affected by factors other than the $i$-layer properties, such as the type of substrate, the $p$-layer quality and thickness, and the $i$-layer thickness.

B. Structural, optical, and electrical properties of solar cells

To compare the properties of the $\mu$-Si:H solar-cell absorber layers grown at different deposition conditions with different growth rates, it is essential to know the structural composition of the $i$ layer. As has been suggested above from the results of the solar cell $J-V$ parameters (Figs. 5 and 8), the variation of power and gas flow under hphP conditions shifts the $\mu$-Si:H/a-Si:H transition considerably to a different silane concentration SC. This shall be confirmed in the following through Raman-scattering experiments performed directly on the solar cells. Knowing the $I_{\text{RS}}^2$ values will allow to compare solar cells at similar crystalline volume fractions but prepared at very different deposition rates.

A further point of concern for solar cell materials prepared at a high deposition rate is that the $i$-layer absorber material might exhibit a structure evolution along the growth axis. The frequently observed interface or incubation layer with pronounced porosity and amorphous phase could be expected to be more developed, i.e., thicker, at higher growth rates. This was investigated in the present research by Raman depth-profile methods.
Finally, the influence of different deposition rates on the electronic and optical properties of the $i$-layer absorber material in the $\mu c$-Si:H solar cell is of interest. These properties, however, are not easily accessible. We shall try to obtain at least some information from the measurements of the dark $J–V$ characteristics and from quantum efficiency measurements.

1. Raman-scattering experiments and structure depth profiles

The $I_C^{RS,488}$ values are shown in Fig. 12 as a function of SC. For the hphP 20-W and hphP 40-W series, only the optimum cells were measured. A decreasing $i$-layer crystallinity with increasing SC can be observed in each series. Depositions with or without a shield around the cathode make no remarkable difference in the structure properties, comparing the hphP 60-W and hphP 100-SCCM series. Although the $\mu c$-Si:H/a-Si:H transition occurs at different SC when different deposition conditions are applied, optimum cells, which can be found between the two dashed lines in this figure, are always obtained at the transition and show a similar crystallinity around 60%. The results confirm the conclusions made from the $J–V$ parameters: An increase of $P_{VHF}$ shifts the $\mu c$-Si:H/a-Si:H transition to higher SC values; an increase of $F_{total}$ shifts this transition to lower SC values. As $R_D$ in all cases increase with SC, such shifts result in corresponding shifts of the deposition rates for optimum solar cells.

The structural development of three series of $\mu c$-Si:H solar cells, hphP 30-W, hphP 60-W, and hphP 100-SCCM, prepared at medium and high deposition rates have been investigated by Raman-scattering measurements with different excitation wavelengths. The results are compared with similar studies of solar cells with standard lplP absorber layers. Figure 13 shows the $I_C^{RS}$ values calculated from a Raman spectra with 647-nm excitation ($I_C^{RS,647}$), plotted against those with 488 nm ($I_C^{RS,488}$). The deviation from the diagonal reflects the structure difference between the positions of the $i$ layer near the etched-away $n$ layer and close to the $p/i$ interface. The lplP samples deposited at a low $R_D$ show a very homogeneous distribution of the crystalline fraction along the growth direction, no matter if highly crystalline or almost amorphous. On the other hand, for the hphP solar cells, the $I_C^{RS,647}$ values are significantly smaller than $I_C^{RS,488}$, indicating a structural evolution during the $i$-layer growth. In particular for the $I_C^{RS,488}$ values around 60% where the optimum cells are obtained (see Fig. 12), a remarkable structure-composition difference between top and bottom can be seen.

But the resolution in growth direction of this method with different wavelengths is, of course, not very high. The $I_C^{RS,647}$ values, considered here to emphasize more the contribution close to the $p/i$ interface, are still strongly affected by the surface-near region. In order to evaluate the crystallinity with a much better resolution at different stages of the $i$-layer growth, Raman measurements with 488-nm excitation were done on craters with different depths, which were etched into the solar cells by KOH. Figure 14 shows the $I_C^{RS,488}$ at different depths measured on the optimum solar cells of selected series. As the solar cells are all about 1-µm thick, positions 0 and 1000 on the $x$ axis correspond to the position of the $n$ and $p$ layers, respectively. Consistent with the “different wavelength” method, the lplP solar cell exhibits its very similar $I_C^{RS,488}$ at different stages of growth, i.e., no structure evolution. For the hphP optimum solar cells, the structure development, already indicated in Fig. 13, is confirmed by this method. $I_C^{RS,488}$ differences of up to 20% between the top and the bottom of the $i$ layer can be observed.

It can be concluded that absorber layers grown with hphP at high deposition rates show considerable structure evolution along the growth axis, while the absorber layer material prepared with a much lower rate under lplP conditions have a very homogeneous structure composition. Sur-
prisingly this does not result in a remarkable deterioration of the solar cell performance. As seen in Fig. 11, \( V_{OC} \) and \( FF \), as a measure of the solar cell performance determined by the \( i \)-layer quality, are independent from the deposition rate.

2. Quantum efficiency

In an attempt to study the influence of structure development on the carrier generation and transport, quantum efficiency measurements were performed on two solar cell series, lplP and hphP 100 SCCM. In general, as the short-wavelength light will be fully absorbed in the \( i \) layer close to the \( p/i \) interface, the short-wavelength response can be considered as the criteria for the \( p \) layer and \( p/i \) interface quality. Long-wavelength light, with a lower absorption coefficient for microcrystalline silicon, will be homogeneously absorbed in the whole 1-µm-thick \( i \) layer. We use the integrated intensity of QE between 300 and 520 nm, \( I_{QE,blue} \) to evaluate the short-wavelength response of solar cells and that between 650 and 1100 nm, \( I_{QE,red} \) for the long-wavelength response. In Figs. 15(a) and 15(b) are \( I_{QE,blue} \) and \( I_{QE,red} \) of the lplP and hphP 100-SCCM series plotted against \( I_{C,RS} \). Consistent with the highest \( J_{SC} \) in the region with intermediate crystallinity around 65% (Figs. 5 and 8), the long-wavelength responses of both series show maximum values in this range [Fig. 15(a)]. At the transition from a highly crystalline to an amorphous growth, the long-wavelength response decreases to lower values with the increasing amorphous phase in the \( i \) layer.

On the other hand, the blue-light response shows a pronounced difference between the lplP and hphP solar cells. In the lplP series, with the exception of the blue response at the highest \( I_{C,RS} \) values, a higher \( I_{QE,blue} \) can be seen in almost the entire \( I_{C,RS} \) range. The differences in the short-wavelength response could be attributed to a deteriorated \( p/i \) interface in the high-deposition-rate material. The presence of a more amorphous or thicker incubation layer, as concluded from the depth-profile methods, could lead to extraction problems for carriers generated near the \( p/i \) interface.

However, the high FF and high \( V_{OC} \) values in these hphP optimum cells indicate that apparently a moderate structure development in the growth direction is not a sufficient reason for bad solar cell performance. Still, a further improvement of the solar cells by an adjustment of the crystallinity at the \( p/i \) interface could be possible.

3. Dark J–V measurements

A further possibility to obtain information about transport and recombination in the \( i \) layers and at the interfaces of the \( p-i-n \) \( \mu c-Si:H \) solar cells is the measurement of the dark \( J–V \) curves. In Fig. 16, the dark \( J–V \) curves of the solar cells of the hphP 100-SCCM series are shown exemplarily. With the decrease of \( I_{C,RS} \) a systematic shift of the curves to lower current densities can be observed, which can also be found in all the other SC series of Table I. According to the simple \( p-n \) diode theory, if the validity of its application to \( \mu c-Si:H \) solar cells is assumed, the decrease in the current density with decreasing \( I_{C,RS} \) qualitatively explains the increase of \( V_{OC} \). Besides the shift of the curves, a change of the slope in the exponential range is also observed. The diode factor \( n \) and saturation current density \( j_0 \) are calculated from the fitting of the exponential part of the dark \( J–V \) curves to the diode equation \( j_{dark}=j_0 [\exp(eV/nkT)-1] \), where shunt and series resistances have minor influence on the dark current density. The results are plotted for various solar cell series prepared at different deposition conditions versus \( I_{C,RS} \) in Fig. 17. With the decrease of the \( i \)-layer crystallinity, the diode factor \( n \) decreases from a value of about 1.85 at high \( I_{C,RS} \) to about 1.4 at low crystalline volume fraction. Although there is some scatter, the values of \( n \) and \( j_0 \) at constant \( I_{C,RS} \) show no systematic dependence on the deposition conditions or \( R_D \) and show no clear trend with the change of deposition parameters. Only the values for the fully amorphous cells prepared at high deposition rates show a clear difference to the low-deposition-rate material. However, the evaluations of the measurement results are likely too ambiguous and based on too simplified assumptions, and therefore should not be overinterpreted.

IV. DISCUSSION

High-efficiency solar cells have been deposited at high deposition rates by the combination of VHF discharge exci-
In the following we shall discuss the influence of the deposition parameters under VHF-hphP conditions on the shift of the crystalline-to-amorphous growth conditions. An illustrative diagram, which considers the ratio of hydrogen over silane radicals as a major parameter, explains the shift of the region for the growth of OPM material. Furthermore, we shall discuss the influence of the high-deposition-rate processes on the material structure and the resulting solar cell performance.

A. Structure adjustment for OPM $\mu$-c-Si:H materials

The various models proposed for the description of $\mu$-c-Si:H growth, such as the partial chemical equilibrium\cite{29} or therewith related to the selective-etching model,\cite{30} the surface diffusion model,\cite{1} and the chemical annealing model,\cite{31,32} have in common that a high hydrogen radical density is considered to be critical for the formation of $\mu$-c-Si:H. A recent study in the VHF-hphP regime shows a good agreement with the above results.\cite{33} To fulfil such conditions, $\mu$-c-Si:H is mostly prepared with a high dilution of the silicon precursor gas, usually silane, with hydrogen together with an effective dissociation of these gases by a high discharge power in PECVD or high filament temperatures in hot-wire chemical vapor deposition (HWCVD). If, in addition, a high growth rate is wanted, a further increase in the dissociation power might be needed. This leads to possible detrimental conditions for the $\mu$-c-Si:H quality by high-energy ion bombardment in PECVD or a possible excess radiative heating in HWCVD. As a possible solution for high-growth conditions of $\mu$-c-Si:H without damage to the surface layer, the high-pressure depletion method was proposed.\cite{3,11} In this approach, the application of a high discharge power is used to decompose most of the silane in initial reactions of the type $\text{SiH}_4 \rightarrow \text{SiH}_3 + (4-x)\text{H}$. Under the silane-depletion condition, the reaction

$$\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2, \quad (1)$$

where silane molecules annihilate atomic hydrogen, will be suppressed and a high atomic hydrogen density is maintained. A high working pressure, which is much higher than the several ten pascals typically used in the conventional RF- or VHF-PECVD techniques for $\mu$-c-Si:H growth, provides sufficient silane molecules and prevents detrimental ion damage. One of the consequences, when working under silane-depletion conditions, is that, if most of the silane molecules are decomposed into growth precursors, one would expect little increase in the deposition rate with an increase in discharge power.

With the results of the present report we can confirm the success of this approach. The results indicate “silane depletion,” at least to some extent, although the term “depletion” is somewhat ambiguous. In how far the silane is depleted is also determined by other deposition parameters, such as the reactor geometry. Note that the increase of $R_D$ with an increase of electrode distance and pressure (Fig. 4) agrees with the assumption of silane depletion. With higher pressure, the total amount of silane in the reaction zone is increased. With higher electrode distance, the volume of the reaction zone

![Graph showing saturation current density $j_0$ and diode factor $n$ vs. $I_{C_{488}}^{RS}$ for solar cells deposited by iplP and hphP.](image)

**FIG. 17.** (a) Saturation current density $j_0$ and (b) diode factor $n$ of the solar cells deposited by iplP and hphP, plotted as a function of $I_{C_{488}}^{RS}$. Optimum cells in different series are generally found between the two dashed lines in the figure. The lines are guides to the eyes.
applied to an established OPM materials-growth condition, a higher $R_D$ will be generally observed because of the higher silane supply (see Fig. 7). But the increasing SiH$_x$ radical and the possible atomic H annihilation effect by the excessive silane molecules result in a lower H/SiH$_x$ ratio, leading to a lower $i$-layer crystallinity. This is confirmed by the Raman-scattering measurements (Fig. 12) and by the $J-V$ parameters (Fig. 8) of the solar cells deposited with different $F_{t_{\text{total}}}$. In order to maintain the proper ratio of atomic H over SiH$_x$, one has to go to a lower SC at a higher $F_{t_{\text{total}}}$; Note that Fig. 18 is just an illustrative picture and the rectangle areas do not represent the true radical densities.

Under high $F_{t_{\text{total}}}$ conditions, the optimum solar cells are prepared at a lower $R_D$ than those at a low $F_{t_{\text{total}}}$ although the total silane flow rate for the optimum cell is still higher. This is an indication of a lower gas utilization under high $F_{t_{\text{total}}}$ conditions, resulting from a shorter gas residence time.

As the variation of SC is the most simple and straightforward method to adjust the H/SiH$_x$ ratio, we consider it mandatory for material and device optimization.

### B. Solar cell performance and $i$-layer properties

The solar cell performance is essentially determined by the $i$-layer properties, if the other cell components, such as substrates and doped layers, are the same for the different solar cells and are not affected by the $i$-layer deposition. We have studied the transport properties of $\mu$-Si:H solar cells prepared by different techniques and at different deposition rates by dark $J-V$ and quantum efficiency measurements and correlated these with the results from Raman and Raman “depth profile” measurements. Based on various earlier reports about high-deposition-rate processes for intrinsic $\mu$-Si:H absorber layers, including work in the hphP regime, one could have expected that the high-rate growth process has a negative influence on the material quality and the structure homogeneity along the growth axis. The results from the structure depth profile clearly show the existence of such a structure inhomogeneity in hphP material at high growth rates. Surprisingly this structure inhomogeneity is not reflected in an overall reduced solar cell efficiency under illumination as compared with a low-deposition-rate material (Fig. 11), but only in a lower short-wavelength response (Fig. 15). Also the evaluations of the dark $J-V$ curves indicate neither differences in the total defect density nor differences in the interface recombination between solar cells prepared with different regimes. Assuming the validity of the theory for $p-n$ diodes as applied to $\mu$-Si:H solar cells, similar defect densities can be deduced from the similar $j_0$ in the solar cells with similar crystallinity and thickness [Fig. 17(a)]. Thus, a similar diode factor $n$ in the solar cells with the same crystallinity [in Fig. 17(b)] suggests no noticeable difference in the recombination at the interface. Detailed discussion about the $j_0$ and $n$ in $\mu$-Si:H $p-i-n$ diodes can be found in Ref. 24. Further-support for similar bulk layer properties between high- (hphP) and low- (lplP) deposition-rate materials is given by the very similar $I_{QE\text{red}}$ values in the quantum efficiency measurements for both types of solar cells.
Another similarity between the lplP and hphP materials is that the optimum solar cells are always obtained at the \(\mu c\)-Si:H/\(a\)-Si:H transition. In good agreement with previous results that a higher defect density was found in the highly crystalline material,\(^{37}\) the reduced \(I_{\text{QE,red}}\) [Fig. 15(a)], the high diode factors \(n > 1.7\), and the high dark saturation current densities (Fig. 17) at the highest crystalline volume fractions suggest carrier extraction problems in the devices. In addition to the higher \(V_{\text{OC}}\) in the solar cells with an OPM material, higher FF in such cells suggests a lower bulk recombination and a better carrier extraction, as compared to the highly crystalline samples.

On the other hand, the considerable difference in blue-light response \(I_{\text{QE,blue}}\) does indicate a difference at the \(p/i\) interface in lplP and hphP solar cells with reduced carrier extraction from the interface-near region in hphP solar cells deposited at high \(R_D\). Although this matches with the observed structure inhomogeneity, the FF remains at high levels above 70%, indicating good carrier extraction from the bulk in these cells.

We summarize that the combination of high plasma-excitation frequencies in PECVD together with high deposition pressures makes it possible to achieve high-rate growth of the OPM material without a negative influence on the solar cell \(J-V\) parameters. All results suggest very good bulk layer properties with no indication for differences between high- and low-growth-rate material. This allows high-rate growth of high-efficiency solar cells. However, there are clear indications for structure inhomogeneity and deteriorated \(p/i\) interfaces in the hphP material. This gives hope for even further improved solar cell performance at high deposition rates by reducing the structure development or improving the \(p/i\) interface.

V. CONCLUSIONS

- A very effective growth regime for the deposition of \(\mu c\)-Si:H solar-cell absorber layers with excellent quality at high deposition rates was identified. It uses VHF-PECVD at high pressure and high power (hphP).
- Under all deposition conditions used, the highest solar cell efficiencies are obtained with optimum phase mixture (OPM) material grown close to the transition from a highly crystalline to an amorphous growth.
- Growth of the OPM material is strongly determined by a proper H over SiH\(_3\) ratio. This ratio is most easily controlled by a variation of the silane concentration. Corresponding silane concentration series are considered mandatory for a successful device optimization.
- The \(\mu c\)-Si:H material quality is found not to be dependent on the deposition rate under VHF-PECVD hphP growth conditions in our investigated regime.
- The structure evolution along the growth axis found for the high-deposition-rate material, though without noticeable effect on the total solar cell efficiency, indicates the potential for further optimization of the presented growth process and the obtained device performance.

ACKNOWLEDGMENTS

The authors thank F. Birmans, M. Hülsbeck, S. Michel, W. Reetz, G. Schöpe, B. Sehrbrock, H. Siekmann, H. Stiebig, and Ch. Zähren, for their constructive contribution to this work.


