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Microcrystalline silicon solar cells with an open-circuit voltage above 600 mV

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Microcrystalline silicon solar cells with an open-circuit voltage surpassing the 600 mV barrier were prepared by combining the use of a hot wire deposited *p-i* interface with that of an *i* layer deposited by radio-frequency parallel plate plasma deposition using controlled SiH₄ flow profiling. The control of the bulk and interface properties facilitated effective charge carrier collection from *i* layers with a crystalline volume fraction as low as $\sim 30\%$. Judging from the absorption in the infrared and the excellent charge carrier transport, the optoelectronic properties of this material were still dominated by the crystalline rather than the amorphous phase. © 2007 American Institute of Physics. [DOI: 10.1063/1.2734375]

Microcrystalline silicon ($\mu\text{c-Si:H}$) consists of ~ 10 nm sized¹ crystalline silicon (*c-Si*) grains embedded in a columnar structure and surrounded by amorphous silicon (*a-Si:H*). The multitude of grain boundaries associated with this heterogeneous material composition makes grain boundary passivation of utmost importance to obtain any electronically high grade material. With respect to application of silicon in solar cells, the grain boundary passivation mainly affects the open-circuit voltage (V_{oc}).² The scientific challenge of controlling the interface passivation thus coincides with the technological development towards higher V_{oc} in solar cells.

Figure 1 shows the progress made in $\mu\text{c-Si:H}$ solar cell technology over the years in terms of the V_{oc} . The first $\mu\text{c-Si:H}$ solar cells, prepared in the 1990s with a crystalline volume fraction typically above 80%, yielded a V_{oc} around 400 mV.^{3–6} In 2000, Vetterl *et al.* presented $\mu\text{c-Si:H}$ solar cells with a lower crystalline volume fraction of 60% that showed an improved V_{oc} of 520 mV.⁷ Even V_{oc} values higher than 520 mV were obtained, for crystalline volume fractions lower than 60%, however, at the cost of a sharp drop in fill factor (FF) and short-circuit current density (J_{sc}). A plausible explanation is that the grain boundaries in the $\mu\text{c-Si:H}$ are increasingly well passivated by the amorphous volume fraction up to a certain threshold fraction. When passing this threshold fraction the optoelectronic properties of the material become *a-Si:H* dominated with a corresponding low hole mobility and low infrared absorption.

For some years it appeared that the V_{oc} at which maximum solar energy conversion efficiency is obtained, the so-called best-cell V_{oc} , was limited to the 520 mV range.^{7–11} However, in 2002 a best-cell V_{oc} of 580 mV was reported for $\mu\text{c-Si:H}$ solar cells prepared by hot wire deposition.¹² For

very high frequency (VHF) plasma-deposited solar cells a best-cell V_{oc} around 570 mV was reported in 2005 by the application of a hot wire (HW) deposited buffer layer between the *p* and *i* layers.¹³ For radio-frequency (rf) plasma deposition, a best-cell V_{oc} around 560 mV was reported in 2005 using a SiH₄ flow profiling technique.¹⁴ Using a similar SiH₄ profiling technique, a best-cell V_{oc} around 570 mV was reported in 2006 for modified VHF deposition.¹⁵ These recent advancements indicate that there is still room for improvement in the technological development towards higher V_{oc} .

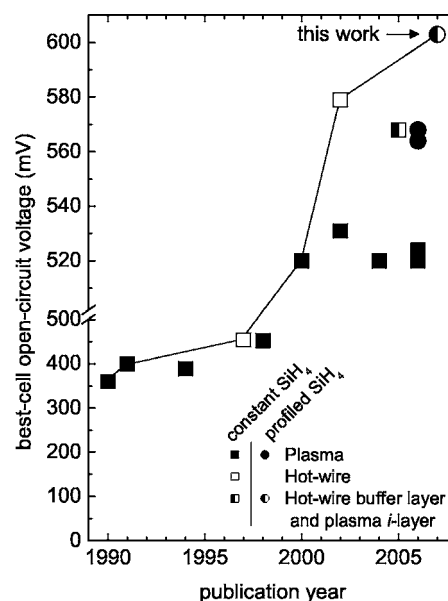


FIG. 1. Progress made in the best-cell V_{oc} of $\mu\text{c-Si:H}$ solar cells for plasma deposition (closed symbols), hot wire deposition (open symbols), and combined hot wire deposition of a buffer layer and plasma deposition of the *i* layer (half-open symbols). Data between 1990 and 1999 concern the initial efforts $\mu\text{c-Si:H}$ solar cells (squares, Refs. 3–6), whereas the data between 2000 and 2006 concern solar cells with $\mu\text{c-Si:H}$ material of optimized crystalline volume fraction (squares, Refs. 7–13). The data using a profiled SiH₄ flow (circles) refer to Refs. 14 and 15 and this work. The solid line connects the best-cell V_{oc} values obtained over time as a guide to the eyes.

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In this letter we report on $\mu\text{c-Si:H}$ solar cells reaching a V_{oc} that surpasses the 600 mV barrier. A best-cell V_{oc} of 603 mV was obtained by a combined approach: (i) controlling the p - i -interface properties using a HW deposited buffer layer and (ii) controlling the i -layer bulk properties by SiH_4 flow profiling during the rf parallel plate plasma deposition process. By this approach the V_{oc} of $\mu\text{c-Si:H}$ solar cells comes closer to the values obtained in the best monocrystalline [706 mV (Ref. 16)], amorphous/crystalline heterojunction [702 mV (Ref. 17)], and multicrystalline [664 mV (Ref. 18)] silicon solar cells. It may thus be regarded as an important step in the progress towards highly efficient thin film silicon solar cells.

The p - i - n solar cells were fabricated on texture-etched ZnO:Al coated glass^{8,19} of $10 \times 10 \text{ cm}^2$ in size. The $\mu\text{c-Si:H}$ p and i layers and $a\text{-Si:H}$ n layers were deposited by 13.56 MHz rf parallel plate plasma deposition in a multi-chamber vacuum system.^{20,21} A second multichamber vacuum system was used for the deposition of $\mu\text{c-Si:H}$ p layers by VHF parallel plate plasma deposition and $\mu\text{c-Si:H}$ buffer layers by hot wire deposition.¹³ For all cells, the i -layer thickness ranged from 1.0 to 1.5 μm . ZnO/Ag back-contacts of $1 \times 1 \text{ cm}^2$ in size defined the aperture area of the solar cells. A class A double-source solar simulator was used for solar cell characterization. Raman scattering measurements were carried out with 647 nm laser light to obtain the semiquantitative measure I_c^{RS} for the average crystalline volume fraction of the i layer, after etching off the n layer with potassium hydroxide. The contribution of the crystalline grains to the Raman scattered signal was determined by subtracting an $a\text{-Si:H}$ reference spectrum.²²

Figure 2 shows the conversion efficiency η , fill factor (FF), and short-circuit current J_{sc} plotted versus V_{oc} for four series of depositions labeled “reference,” “hot wire buffer,” “ SiH_4 profiling,” and “buffer+profiling.” The different values for the V_{oc} in each series were obtained by varying the (time-averaged) SiH_4 flow at which the i layer was deposited. The measured solar cell and film properties at the best-cell V_{oc} are stated in the legend. The reference series was prepared without vacuum break in the H_2 diluted rf high pressure depletion regime.^{20,21} In the hot wire buffer series, a hot wire deposited buffer layer with a thickness of $\sim 15 \text{ nm}$ was prepared under low pressure, low deposition rate, low filament temperature conditions,¹³ while, after transport through air, the i and n layers were deposited under equal conditions as for the reference series. Since the VHF deposited p layer in these cells was slightly thinner than the p layer in the reference series, the current for this series was slightly higher and the fill factor slightly lower. The SiH_4 profiling series was rf deposited using an undiluted feed gas flow (i.e., consisting solely of SiH_4) that was gradually increased during deposition by $\sim 20\%$ in order to keep the plasma’s optical emission intensity constant.¹⁴ In the buffer+profiling series, deposition of the p layer and HW buffer layer took place under equal conditions as the hot wire buffer series whereas the deposition of the i and n layers took place under equal conditions as the SiH_4 profiling series.

For each series in Fig. 2 one can clearly distinguish a best-cell V_{oc} at which maximum solar energy conversion efficiency is obtained. Application of the HW buffer layer and application of the controlled SiH_4 profiling technique both enhance the best-cell V_{oc} , from 533 mV for the reference series to 550 and 564 mV for the hot wire buffer and SiH_4

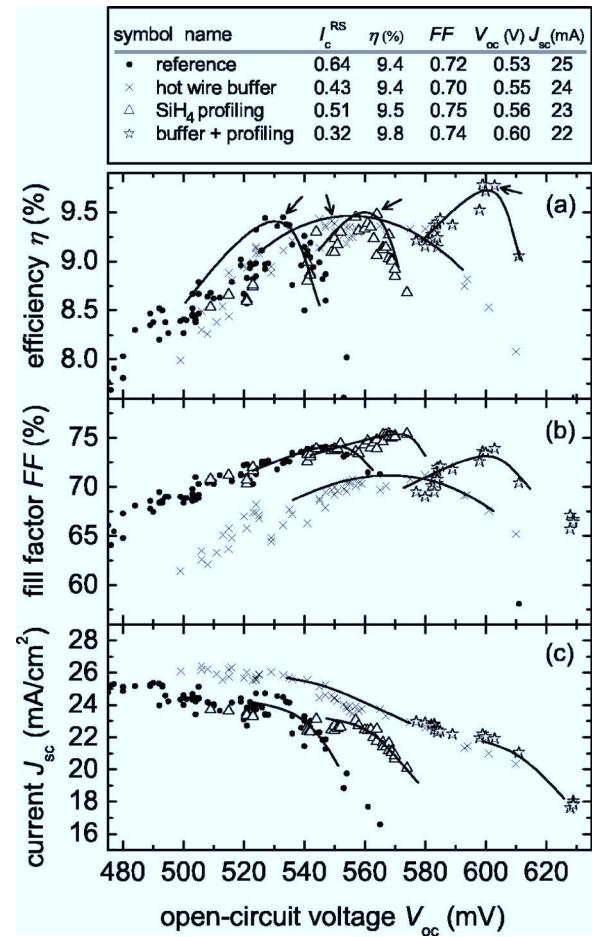


FIG. 2. Solar cell parameters: (a) efficiency η , (b) fill factor (FF), and (c) short-circuit current density J_{sc} vs the open-circuit voltage V_{oc} , in a reference series using rf plasma deposition (dots), incorporating a hot wire deposited buffer layer (crosses), incorporating controlled SiH_4 flow profiling (triangles), and incorporating both a hot wire deposited buffer layer and controlled SiH_4 flow profiling (stars). The trends of the four series around the best-cell V_{oc} are indicated by solid lines as a guide to the eyes. The legend summarizes the best-cell parameters for the solar cells indicated by arrows in (a).

profiling series, respectively. The Raman characterization indicates that in both series the enhanced best-cell V_{oc} is accompanied by a decrease in best-cell I_c^{RS} , from 64% for the reference series to 43% and 51% for the hot wire buffer and SiH_4 profiling series, respectively.

By simultaneously applying a HW buffer and controlled SiH_4 profiling a best-cell V_{oc} of 603 mV was obtained with a best-cell I_c^{RS} of 32%. The reasonably good red and near infrared absorption ($J_{\text{sc}} = 22 \text{ mA/cm}^2$) and excellent electronic transport properties (FF=74%) indicate that the optoelectronic properties of this material were still determined by the crystalline rather than the amorphous volume fraction. Figure 3 compares the external quantum efficiency (EQE) for cells with different V_{oc} values. From Fig. 3(a) it is evident that in the reference series, both blue and near infrared responses drop sharply above the best-cell V_{oc} of 533 mV. By the application of the hot wire buffer and the SiH_4 profiling, the drop in blue response is prevented completely and the drop in the near infrared is reduced significantly. One may thus tentatively conclude that the hole collection near the p - i interface and the hole mobility near the i - n interface have significantly been improved, thus allowing the efficient

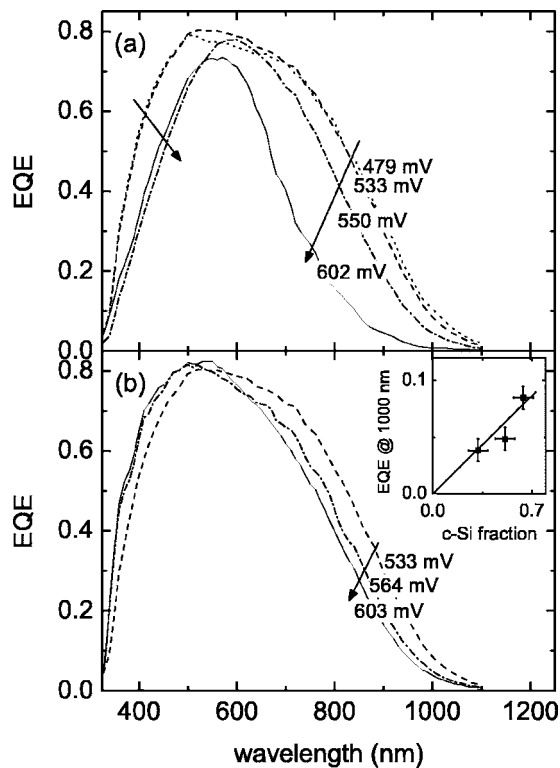


FIG. 3. Comparison of the external quantum efficiency (EQE) of solar cells with various open-circuit voltages: (a) cells from the “reference” series and (b) best cells from the reference, “SiH₄ profiling,” and “buffer+profiling” series. The inset in (b) shows the EQE at 1000 nm as a function of the crystalline volume fraction of the *i* layer.

charge carrier collection at this low crystalline volume fraction of 32%.

In contrast to the collection efficiency, the generation of charge carriers was not maintained at low crystalline volume fraction. Namely, Fig. 2 indicates that throughout all four data series there is a trend of decreasing J_{sc} with increasing V_{oc} . Figure 3(b) and inset show that this trend originates from a linearly decreasing infrared response with decreasing crystalline volume fraction. We may conclude that the high amorphous volume fraction that is necessary to obtain a high V_{oc} simultaneously results in a lower J_{sc} .

Finally, from the high amorphous volume fraction of the best solar cell from the buffer+profiling series one might expect considerable light induced degradation. For solar cells with a crystalline volume fraction of 30%–40% Klein *et al.*,²³ who investigated hot wire deposited solar cells, and Wang *et al.*,²⁴ who investigated plasma-deposited solar cells with hot wire buffer layer, both found a degradation in efficiency of around 8% after 1000 h of AM 1.5 white light illumination under open-circuit conditions. We therefore expect the degradation of the solar cells presented in this work to lie in the same range. In this respect it is important to point out that the single junction μ c-Si:H degradation does not hold clear consequences for degradation of a μ c-Si:H bottom cell in a tandem structure. Namely, a bottom cell would receive considerably less blue and green light. Absorption in this case will take place mainly in the crystalline volume fraction. Since it is energetically highly unfavorable for charge carriers that are generated within the crystalline volume fraction, no charge carrier tail-to-tail recombination should take place within the amorphous volume fraction of a

bottom cell. One may thus expect a bottom cell to be more stable during light soaking than a single junction cell.

In summary, single junction μ c-Si:H solar cells with a solar energy conversion efficiency of 9.8% and a V_{oc} of 603 mV were obtained through a combination of a hot wire buffer layer (affecting the *p-i* interface) and controlled SiH₄ flow profiling (affecting the bulk *i* layer). The obtained material with a low crystalline volume fraction of $\sim$ 30% shows excellent electronic properties and is a promising candidate for use in μ c-Si:H applications.

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