Comparison of amorphous silicon absorber materials: Light-induced degradation and solar cell efficiency
M. Stuckelberger, M. Despeisse, G. Bugnon, J.-W. Schüttauf, F.-J. Haug, and C. Ballif

Citation: Journal of Applied Physics 114, 154509 (2013); doi: 10.1063/1.4824813
View online: http://dx.doi.org/10.1063/1.4824813
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/114/15?ver=pdfcov
Published by the AIP Publishing
Comparison of amorphous silicon absorber materials: Light-induced degradation and solar cell efficiency

M. Stuckelberger,a) M. Despeisse, G. Bugnon, J.-W. Schüttauf, F.-J. Haug, and C. Ballif
Ecole Polytechnique Fédérale de Lausanne (EPFL), Photovoltaics and Thin-Film Electronics Laboratory,
Rue de la Maladière 71B, CH-2000 Neuchâtel, Switzerland

(Received 18 August 2013; accepted 25 September 2013; published online 16 October 2013)

Several amorphous silicon (a-Si:H) deposition conditions have been reported to produce films that degrade least under light soaking when incorporated into a-Si:H solar cells. However, a systematic comparison of these a-Si:H materials has never been presented. In the present study, different plasma-enhanced chemical vapor deposition conditions, yielding standard low-pressure VHF a-Si:H, protocrystalline, polymorphous, and high-pressure RF a-Si:H materials, are compared with respect to their optical properties and their behavior when incorporated into single-junction solar cells. A wide deposition parameter space has been explored in the same deposition system varying hydrogen dilution, deposition pressure, temperature, frequency, and power. From the physics of layer growth, to layer properties, to solar cell performance and light-induced degradation, a consistent picture of a-Si:H materials that are currently used for a-Si:H solar cells emerges. The applications of these materials in single-junction, tandem, and triple-junction solar cells are discussed, as well as their deposition compatibility with rough substrates, taking into account aspects of voltage, current, and charge collection. In sum, this contributes to answering the question, “Which material is best for which type of solar cell?” © 2013 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4824813]

I. INTRODUCTION

Since the discovery of the Staebler-Wronski effect in 1977,1 light-induced degradation of hydrogenated amorphous silicon (a-Si:H) has been widely discussed in the literature. Nevertheless, the processes that lead to (partially reversible) deteriorated conductivity and enhanced recombination in solar cells are not yet fully understood at the atomic and energy-band levels. Thus, light-induced degradation remains an active field of research for a-Si:H solar cells. Several models exist that explain aspects of light-induced degradation, see, e.g., the review article.2 Recently, the role of vacancies and voids in light-induced degradation has received increased attention.3–5

Leading institutes in the development of a-Si:H solar cells have claimed different plasma-enhanced chemical vapor deposition (PECVD) conditions for a-Si:H absorber materials to be best suited for high-efficiency solar cells showing high efficiency (with low light-induced degradation). These material classes include:

- Low-pressure VHF a-Si:H: Deposited at low pressure and very high frequency (VHF) (typically 0.2–0.8 mbar, 40–140 MHz) with rather low hydrogen dilution, these materials have small bandgaps and provide high currents, mainly for use in single-junction or micromorph tandem solar cells.6,7
- Protocrystalline silicon (pc-Si:H): Deposited at moderate pressure and radio frequency (RF, 13.56 MHz) with a hydrogen dilution close to the transition from a-Si:H to microcrystalline silicon (µc-Si:H), these materials have a wide bandgap for triple-junction solar cells. If grown thick enough, this material can turn into µc-Si:H with increasing crystallinity.8–10
- Polymorphous silicon (pm-Si:H): The deposition conditions of pm-Si:H are close to those of pc-Si:H, but possibly a slightly higher pressure is used. In contrast to pc-Si:H, this material can be grown thick without a transition to µc-Si:H. Small crystallites, produced in the plasma phase, can be distributed homogeneously throughout the thickness as these deposition conditions are close to the powder regime.11,12
- High-pressure RF a-Si:H: These materials are deposited at high pressures (typically above 6 mbar) and RF, often with a smaller inter-electrode gap.13,14
- Triode: Deposition conditions similar to low pressure VHF a-Si:H but with an additional biased mesh between the electrodes lead to very low deposition rate but dense material.15,16

a-Si:H deposition techniques other than PECVD, such as sputtering,17 hot-wire deposition,18,19 or expanded thermal plasma deposition20 did not lead to high solar cell efficiencies or were not commercially practical, and will not be discussed here further.

In this contribution, we present a systematic study of different deposition conditions in order to sweep through the range of a-Si:H materials listed above. We restricted our study to PECVD with two electrodes, and only silane and hydrogen were used as gaseous precursors. We varied the hydrogen dilution, pressure, power, and excitation frequency...
of the plasma during the deposition of $a$-Si:H films incorporated as the absorber in single junction solar cells.

II. EXPERIMENTAL

A. Deposition conditions for intrinsic $a$-Si:H

All silicon layers were deposited by PECVD in an Octopus I cluster tool developed by INDEOtec SA, which allowed a wide variety of deposition conditions and fast equilibration times thanks to a closed reactor design.22

The symmetric electrodes in each chamber were $15 \times 16$ cm$^2$, the inter-electrode gap was 15 mm, and the excitation frequency was 13.56 MHz fixed or adjustable (VHF). Dedicated chambers were used for $p$-layer, $n$-layer, and $i$-layer depositions, and different chambers were used for $i$-layers deposited at RF and VHF.

Table I summarizes the deposition parameters of the four plasma regimes investigated in this study. For each of these regimes, the hydrogen dilution was widely varied while keeping the total gas flow constant. Exceptions for very high or low dilutions were made due to limitations of the mass flow controllers. Note that the power was measured at the generator output.

The deposition temperature was kept at 200 °C. For the best bulk material quality in the different pressure regimes, we chose the lowest power density that allowed plasma ignition for all hydrogen dilutions. Temperature and power series for selected deposition conditions complete the explored parameter space.

B. Solar cell design

The $a$-Si:H films described in Sec. II A were incorporated into solar cells. We used the same cell design (see Fig. 1) for all experiments and changed only the intrinsic bulk layer to obtain a direct comparison of bulk layer properties resulting from the investigated deposition conditions.

The $a$-Si:H solar cells were deposited in the superstrate configuration ($p-i-n$) on 0.5 mm thick Schott AF 32 glass substrates. For the front and back contacts, 2 μm thick boron-doped ZnO ($ZnO:B$) was deposited by low-pressure chemical vapor deposition (LPCVD). All solar cells were co-deposited on four different substrates with varying roughness: Three substrates consisted of co-deposited ZnO:B on glass. On one, as-deposited ZnO:B was used; on two others, the ZnO:B was treated for 4 and 10 min with an argon plasma to smoothen the surface texture from V- into U-shaped. This leads to not only less shunting but also less light scattering.23 All results shown below except in Sec. III F refer only to the substrate treated for 4 min. The presented trends, however, were consistent across all substrates. As a flat reference, a fourth substrate with smoothly grown LPCVD ZnO:B was used, also treated for 4 min with an argon plasma.24,25

Solar cell deposition began with a $p$-type bilayer. Directly on the ZnO, we deposited a microcrystalline silicon-oxide layer ($p-(μ-SiO:H)$) for good electrical contact, enhanced transparency, and shunt-quenching.26,27 This was followed by an amorphous silicon carbide layer ($p-(a-SiC:H)$) with a wide bandgap to provide a high electric field. The $p$-type layers were deposited at nominally 150 °C and 40.68 MHz.

In order to keep the sensitive $p$-$i$ and $i$-$n$ interfaces as similar as possible from one deposition to the other, we sandwiched the 220 nm thick intrinsic bulk absorber layer under investigation between 10 nm thick intrinsic $a$-$Si:H$ buffer layers at both interfaces, deposited at 200 °C, RF, and high hydrogen dilution. These buffer layers (as well as the doped layers and ZnO contacts) were the same on all solar cells, regardless of the intrinsic bulk layer. The deposition conditions were chosen right at the transition from $a$-$Si:H$ to $μ$-$Si:H$ but still amorphous enough that the buffer layer grew amorphous even on $μ$-$Si:H$.

The three $i$-layer depositions were followed by an $n$-type bilayer consisting of an amorphous silicon layer ($n-(a-Si:H)$) and a microcrystalline silicon oxide layer ($n-(μ-SiO:H)$) in contact with the back ZnO:B. They were deposited at 200 °C and 40.68 MHz.

In addition to SiH$_4$ and H$_2$, CO$_2$ was used for oxide layers, B(CH$_3$)$_3$ for $p$-type layers, PH$_3$ for $n$-type layers, and CH$_4$ for the carbide layer. For better reproducibility and to ensure that cell performance was not limited by the doped layers, all doped layers were thicker than those in cells optimized for high efficiency.

For each substrate, an array of 16 cells, each 0.25 cm$^2$ in size, was defined and polytetrafluoroethylene (PTFE) was used as a white back reflector.

<table>
<thead>
<tr>
<th>Pressure (mbar)</th>
<th>Power (W)</th>
<th>Total gas flow (sccm)</th>
<th>Frequency (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>3</td>
<td>30</td>
<td>40.68</td>
</tr>
<tr>
<td>2.5</td>
<td>3</td>
<td>85</td>
<td>13.56</td>
</tr>
<tr>
<td>5.0</td>
<td>10</td>
<td>100</td>
<td>13.56</td>
</tr>
<tr>
<td>9.0</td>
<td>20</td>
<td>100</td>
<td>13.56</td>
</tr>
</tbody>
</table>

FIG. 1. Solar cell structure used for all $p-i-n$ solar cells.
C. Layer and cell characterization

For measurements of intrinsic bulk layer properties, the layers were deposited on 0.5 mm thick Schott AF 32 glass substrates and 250 μm thick double-side polished intrinsic (100) crystalline silicon (c-Si) wafers.

Ellipsometry measurements were performed using a UVISEL ellipsometer from Horiba Jobin Yvon (with monochromators for IR and UV/Vis) between 0.6 and 6 eV, and transmission measurements using a Lambda 900 spectrometer from Perkin Elmer between 300 and 2000 nm. For Fourier transform infrared (FTIR) spectroscopy measurements, a Spectrum 2000 spectrometer from Perkin Elmer and a Nicolet 8700 spectrometer from Thermo Scientific were used. Raman crystallinity was measured on an Invia Raman microscope from Renishaw and on a Senterra Raman microscope from Bruker with green lasers.

Current-voltage (I-V) characteristics were measured with a four-lamp solar simulator from Wacom (class AAA) under standard conditions (AM1.5g, 1000 W m\(^{-2}\), 25 °C).\(^{28,29}\) Current was determined from an external quantum efficiency (EQE) system built-in-house. Light soaking was performed in a sun simulator from Solaronix (class AAA) under standard conditions (AM1.5g, 1000 W m\(^{-2}\), 50 °C).\(^{30}\)

III. RESULTS AND DISCUSSION

A. Plasma regimes

Figure 2 shows the lowest power for pure silane and hydrogen plasmas (both for RF and VHF) for which a stable plasma could be sustained. Instead of the breakdown voltage that is more commonly shown for Paschen curves,\(^{31}\) we show here the extinction power as it is more relevant for the deposition of layers. This graph gives an overview of the characteristics of our reactor and the deposition conditions that are accessible. The curves for RF are less smooth than those for VHF because of the amplifier precision limit of 1 W. In further discussion, we refer to the "turning point"\(^{32}\) as the lowest pressure at which the plasma could be sustained, and to the "diffusion/drift" branch as the part of a Paschen curve at pressures significantly above the pressure of minimum extinction power.

Four observations are relevant for a-Si:H deposition from silane/hydrogen plasma by PECVD:

(i) At high pressures, higher power is needed when the frequency is increased from 13.56 to 40.68 MHz.
(ii) At high pressures, higher power is needed for SiH\(_4\) than for H\(_2\).
(iii) VHF sustains plasmas at much lower pressures than RF.
(iv) SiH\(_4\) plasmas can be sustained at lower pressures than H\(_2\) plasmas.

Assuming vanishing electron concentrations close to the electrodes, the extinction power at high pressures is limited by the ionization rate \(\nu_1\) of gas molecules via electron impact:

\[
\nu_1 = \alpha + \beta \cdot (L - 2A)^{-2}.
\]

Here, \(\alpha\) and \(\beta\) are constants that include the reactor size and electron diffusion coefficients, \(L\) denotes the inter-electrode gap and \(A = V_{dr}/(2\pi f)\) is the electron displacement amplitude expressed in terms of the electron drift velocity \(V_{dr}\) and the RF field frequency \(f\).

From Eq. (1), we see that an increase of the frequency leads to a lower electron displacement amplitude and a lower ionization rate. Hence, a stronger electric field may be needed for the electrons to acquire sufficient energy to perform electron-impact ionization of molecules, which may explain why a higher power is needed to sustain VHF plasmas, as observed in (i).

In contrast, Eq. (1) is not valid close to the turning point, where the mean free path of the electrons is of the same order as the inter-electrode distance, \(L \approx 2A\), and electron loss at the electrodes limits the plasma-sustaining conditions. With increasing frequency (lower \(A\)), fewer electrons are lost at the electrodes and the plasma can be sustained at lower pressures; this explains (iii).

Similar reasoning explains (iv): A SiH\(_4\) plasma can be operated at lower pressures compared to a H\(_2\) plasma due to a higher dissociation cross section and hence lower mean free path of the electrons.

Observation (ii) has already been reported elsewhere.\(^{35,36}\) For a given pressure, more electrons are lost in collisions in a SiH\(_4\) plasma than in a H\(_2\) plasma; hence, a higher power is needed.

The differences between H\(_2\) and SiH\(_4\) plasmas and the crossing of their Paschen curves are of great importance for depositions at low power as is desired for highly stable solar cells:

(a) For low pressures, hydrogen dilution can make it impossible to sustain a plasma, while at high pressures it allows a plasma to be sustained at a lower power.
(b) For low pressures, where electron loss at the electrodes dominates, ignition with an external electron source can reduce the ignition power dramatically. However, this has hardly any effect at higher pressures, where electron loss by collisions in the gas phase limits the plasma ignition. More concretely, the plasmas for the hydrogen dilution series at 0.2 mbar were ignited with...
the help of an external electron source, while only slightly higher power but no external charges were required for the ignition of the plasmas in the dilution series at 2.5, 5.0, and 9.0 mbar.

B. Deposition rates

The deposition rates of the investigated plasma conditions are shown in Fig. 3. For each hydrogen dilution series (see Fig. 3(a)), one can distinguish two different branches: The deposition rate increases with increasing hydrogen dilution at low dilution, and seems to decrease logarithmically at high dilution.

At low hydrogen dilutions, powder formation with non-uniform deposition of the layer is observed. Hence, the deposition rate is lowered by polymerization of SiH₄ towards higher silanes that are pumped away and do not contribute to the growing film.

The deposition rates of the investigated plasma conditions, the deposition rate $r$ should be proportional to the concentration $c_{SiH_4}$ of the main film precursor in the plasma, SiH₃, which in turn depends on $N_{e3}$, the number of electrons with a sufficiently high energy to initiate the SiH₄ → SiH₃ + H reaction. The electron impact energy needed for this reaction path (8.75 eV) is close to the dissociation energy of molecular hydrogen (8.85 eV).

Thus, the number of electrons used for silane dissociation is proportional to $N_{e3}$ and we conclude that

$$r \propto c_{SiH_4} \propto N_{e3} \cdot \frac{\Phi_{SiH_4}}{\Phi_{SiH_4} + \Phi_{H_2}} \propto P \cdot \frac{\Phi_{SiH_4}}{\Phi_{SiH_4} + \Phi_{H_2}} = P_{SiH_4}.$$  

The deposition rate as a function of the partial power is plotted in Fig. 4. Indeed, we see that the deposition rate increases linearly with the partial power for low $P_{SiH_4}$. Note that the curves for different pressures and powers overlap well within experimental error.

The temperature dependence of the deposition rate is weak as can be seen in Fig. 3(b). However, it was systematically observed for different pressures and dilutions that the deposition rate increases with increasing temperature, in agreement with measurements by Andújar et al. (For the triode reactor configuration, where we expect the temperature dependence of the deposition rate to be similar to that in diode configuration, such a temperature dependence was not seen within the temperature range of interest). We suggest the following explanation: With increasing temperature, the desorption rate of hydrogen from the surface is higher, and hence less hydrogen is available at the surface. At the same time, more dangling bonds provide “sticking places” for film precursors, thus leading to a higher deposition rate. One may imagine that powder formation could also be responsible: There tends to be less powder at higher temperatures; therefore, the deposition rate could be higher because fewer film precursors are lost to powder. Further,
following the ideal gas law, a higher temperature means a lower gas number density, and hence fewer gas-phase collisions and less powder. However, no powder formation was observed for the layers presented in Fig. 3(b) or for other series in which this temperature dependence was observed. Therefore, we conclude that powder formation does not play a major role in the deposition rate increase with temperature.

In Fig. 3(c), we see that the deposition rate increases linearly with power for depositions at VHF, 0.2 mbar, and a H2:SiH4 flow ratio of 1:1. This confirms that the deposition rate is indeed limited by silane dissociation.

C. Bandgap

Optical layer characterization was performed by combined fitting of three-angle ellipsometry measurements and transmission measurements of layers deposited on glass with a Tauc-Lorentz model, taking into account surface roughness. The bandgaps—parametrized here by the model-independent energy $E_{\text{opt}}$, at which the absorption coefficient reaches $10^4$ cm$^{-1}$—of the dilution series for different pressures are shown in Fig. 5. Other bandgap parametrizations like the Tauc-Lorentz bandgap $E_{\text{TL}}^\text{T}$ or the Tauc bandgap $E_{\text{TL}}^\text{V}$—all determined from fits to ellipsometry and transmission data—show the same trends. For higher hydrogen dilutions than those shown here, Raman measurements showed a crystalline peak at around 520 cm$^{-1}$; in these cases, the fitting of the ellipsometry/transmission data with a single Tauc-Lorentz oscillator was no longer adequate and the measurements are not shown here. Thus, the data at the highest hydrogen dilution mark the transition from a-Si:H to $\mu$-c-Si:H. Note that the hydrogen dilution at which the transition takes place increases with increasing pressure due to decreased ion bombardment on the surface and hence a lower surface mobility of the adatoms.

As reported elsewhere, the bandgap increases with increasing hydrogen dilution—moderately at low dilutions and stronger close to the transition. Whether this is due to a depletion of states close to the valence band, decreased structural disorder, to compressive stress associated with hydrogen incorporation in divacancies and nanosized voids, or to a combination of these effects is not clear.

D. Solar cell performance after light soaking

The solar cell results reported in this section are taken from the cell on each substrate with the highest $V_{\text{oc}} \times FF$ product in the initial state (with $V_{\text{oc}}$ the open circuit voltage and $FF$ the fill factor). These cells are most often also the best on their respective substrate after light soaking.

Differences among various absorber layers are often visible only after light soaking, when the conversion efficiency is typically limited by electron/hole recombination at light-induced defects. Therefore, initial solar cell performance is not shown here, and we instead concentrate on solar cell performance after light soaking and the relative light-induced degradation.

The performance of solar cells (in terms of $V_{\text{oc}}$, $FF$, short-circuit current density $J_{\text{sc}}$, and conversion efficiency) with the $i$-layers that have been discussed in Secs. III A–III C is shown in Fig. 6. As expected from the layer properties of the bulk absorber material, $V_{\text{oc}}$ increases generally with hydrogen dilution due to a bandgap increase (see Fig. 6(a)), until it drops sharply as soon as nanocrystals start to grow near the $i$-$n$ interface at the transition to $\mu$-c-Si:H. The highest $V_{\text{oc}}$ that can be obtained by varying the hydrogen dilution for a given pressure increases with pressure (emphasized with black circles in Fig. 6(a)). This can be partially explained by the increased bandgap of the corresponding layers as shown in Fig. 5. In addition, the decreased ion bombardment of the underlying $p$- and buffer layers at the beginning of the $i$-layer deposition could create fewer defects at the $p$-$i$ interface.

In Fig. 6(c) we see that the increased bandgap with dilution leads to a decreased current due to less absorption of low-energy photons, consistent with Figs. 5 and 6(a). At very high dilutions, where crystallites start to grow near the $i$-$n$ interface, the current drops quickly due to poor collection of charge carriers that are excited in the crystalline phase (too high barrier for holes at the crystalline/amorphous interface). However, these charge carriers generated from photons at wavelengths above 750 nm are collected in quantum efficiency measurements under reverse-bias voltage.

![Diagram](image-url)
For the combination of very low hydrogen dilutions and high pressures, the current is lower than expected from the bandgap of the absorber layers. The difference between external quantum efficiency measurements performed under 1 V bias voltage (EQE(1 V)) and without any bias voltage (EQE(0 V)) shows that in these cases there is a large collection problem over the entire absorption spectrum but it is accentuated for blue light. Further, visual inspection of the corresponding layers and substrate holders showed powder deposition. These two observations support the hypothesis that a-Si:H deposited under these conditions contains many defects and is porous.

Further, visual inspection of the corresponding layers and substrate holders showed powder deposition. These two observations support the hypothesis that a-Si:H deposited under these conditions contains many defects and is porous. The poor material quality resulting from high-pressure and low-hydrogen-dilution depositions affects the FF even more than the J_sc as we see to the left of the maximum (for low hydrogen dilutions) in Fig. 6(b).

Figure 6(d) shows the conversion efficiencies of the solar cells calculated from the Voc, J_sc, and FF values shown in Figs. 6(a)–6(c). It shows the trade-off between high voltage (wide-bandgap absorber), high current (small-bandgap absorber), and high FF (good charge collection). As the FF varies most for the different deposition conditions, trends in efficiency mainly reflect trends in FF, which turns out to be the most crucial parameter when optimizing solar cell efficiency.

In contrast to United Solar Systems Corp.’s successful industrial production of top cells for n-i-p triple junctions with wide-bandgap absorbers and good charge collection,9 it is questionable whether wide-bandgap absorber materials are well suited for high-efficiency solar cells in the p-i-n configuration. For a-Si:H single junction solar cells as well as for a-Si:H top cells in micromorph solar cells, the current that is needed in the a-Si:H cell for a high-efficiency solar cell cannot be obtained with a wide-bandgap absorber layer, as an increase of Voc × FF can never compensate for the lower current. For top cells in triple-junctions, it is not clear whether a wide-bandgap top cell (higher Voc/FF but lower current and thicker; hence stronger light-induced degradation) is suitable for high-efficiency solar cells.
degradation), or a small-bandgap top cell (lower $V_{oc} \times FF$ but higher current; can be made thinner and hence lower light-induced degradation), gives better performance. This depends on the quality of each layer and on the roughness of the used substrate (see discussion in Sec. III F).

Overall, it is important to note that with increasing pressure, the process window within which high-efficiency solar cells can be obtained gets smaller. Even hydrogen dilutions that are not very far away from the transition from $\alpha$-Si:H to $\mu$-Si:H tend to lead to powdery plasmas and poor material quality.

Note that we did not optimize the doped layers for record efficiency, nor adapt them to different $i$-layer process pressures. Nevertheless, efficiencies above 7.5% were obtained for each processing pressure and the best cells without an antireflective coating reached a very high efficiency of 8.7% with a $FF$ of 68% after light soaking.

E. Relative light-induced degradation

Figures 7(a) and 7(b) show the relative light-induced degradation of the $FF$:

$$\Delta FF = \frac{FF_{after \ light \ soaking} - FF_{before \ light \ soaking}}{FF_{before \ light \ soaking}}$$

and of the conversion efficiency. Most trends observed in Fig. 6 are reproduced here, which reflects the fact that the $i$-layer quality governs the initial state less than the light-soaked state. Moreover, the $FF$ is the parameter that dominates the efficiency after light soaking. We see that cells deposited under higher pressure degrade more, especially for low hydrogen dilutions. For lower pressures, there is a wider range of dilutions that provides low-degradation cells than for higher pressures. However, at all pressures there is an optimum hydrogen dilution for which the cells degrade only about 15%, which is remarkably low. These solar cell results are in accordance with the conclusions from plasma and layer analysis.

A correlation between light-induced degradation and the microstructure factor

$$R' = \frac{HSM}{LSM + HSM}$$

has been reported elsewhere, where HSM and LSM are the integrals of the fits of the high and low hydrogen stretching modes around 2090 cm$^{-1}$ and 2000 cm$^{-1}$, respectively.

For all layers investigated in the present article, the stretching mode absorption bands (hence $R'$) have been measured by FTIR and fitted with two Gaussians after correction with a linear baseline. In all series except 0.2 mbar, $R'$ shows a minimum (see Fig. 8). The range of small $R'$ becomes narrower and more pronounced as the pressure is increased (note the logarithmic scale). The broad minimum of low $R'$ for low pressures is consistent with the conclusions from plasma and layer analysis.

In our case, the light-induced degradation of the cells follows the trends of $R'$, as can be seen comparing Fig. 8 with Fig. 7. For low pressures, $R'$ does not depend much on the hydrogen dilution up to the transition to $\mu$-Si:H growth. In contrast, $R'$ strongly depends on the hydrogen dilution for higher pressures which can be attributed to the powdery deposition conditions that result in larger voids and more SiH$_n$ bonds with $n \geq 2$.

F. Substrate dependence of $V_{oc}$

Until now, the substrate dependence of cell parameters was not addressed because the discussed trends were
observed for all substrates. Nevertheless, solar cell performance, and in particular $V_{oc}$, can depend strongly on the substrate roughness. In Fig. 9, $V_{oc}$ is shown for cells co-deposited on four different substrates for the hydrogen dilution series deposited at 5.0 mbar. For all other hydrogen dilution series (variable pressure, deposition temperatures of 160 and 250°C), the same trends were observed.

For low hydrogen dilutions, $V_{oc}$ decreases only slightly with increasing roughness. At least two mechanisms can lead to this substrate dependence: First, the surface area of a rough substrate is larger than that of a smooth substrate, leading to thinner doped layers. Second, non-conformal or even non-homogeneous deposition on a rough substrate leads to a higher probability that the front and back electrode may be nearly touching or may be poorly covered by the doped and intrinsic layers. This can introduce weak diodes (parallel to the standard diode in an equivalent circuit) that lower $V_{oc}$. (Note that, in this substrate dependence, these zones may create weak diodes that lead to a lower current, and thus wide-bandgap materials deposited at high dilution are not optimal for a-Si:H single-junction or micromorph tandem devices.

**IV. CONCLUSIONS**

Using VHF and RF PECVD, intrinsic a-Si:H layers were deposited in a single deposition system varying hydrogen dilution, pressure, temperature and power, covering low-pressure VHF a-Si:H, protocrystalline, polymorphous and high-pressure RF a-Si:H materials. This allowed for the first time a direct comparison of these materials regarding their optical properties and the performance of solar cells using them as absorber layers. The plasma physics was discussed to explain the differences observed.

While optimum hydrogen dilutions leading to relative light-induced degradation below 15% were identified for all process pressures, the process windows leading to such results narrow for increasing deposition pressure due to powder plasmas at low dilutions. The best cells reach post-light-soaking efficiencies of 8.7% and FF of 68% without an antireflective coating.

Light-induced degradation was shown to correlate well with the microstructure factor $R^*$, which has a sharp minimum for high pressures but depends only little on the hydrogen dilution for lower pressures.

While the same trends were observed for cells co-deposited on four substrates with different roughnesses, their sensitivity changed considerably with the substrate roughness. In particular, the substrate dependence of $V_{oc}$ increases dramatically from about 10 to 40 mV after light soaking but grows microcrystalline after a few hundred nanometers in the 1-μm thick solar cell. A transmission electron microscope (TEM) image of the thick cell is shown in Fig. 10. It reveals substrate-dependent porous zones, seen as chains of voids located above peaks of the underlying ZnO texture and highlighted by arrows in the figure. These zones could create weak diodes similar to porous zones in µc-Si:H and thus decrease $V_{oc}$. (Note that, in µc-Si:H, porous zones are located above ZnO valleys.) Further investigations of these zones are ongoing.

While the increased dependence on substrate roughness for high hydrogen dilutions is less an issue for triple junctions, where one can use wide-bandgap a-Si:H materials together with smoother substrates, one needs better light trapping for single-junction or micromorph tandem devices and hence rougher substrates. However, on rougher substrates, the bandgap increase (compared to lower hydrogen dilutions) is not fully reflected in the $V_{oc}$. The slightly increased $V_{oc}$ does not compensate for the lower current, and thus wide-bandgap materials deposited at high dilution are not optimal for a-Si:H single-junction or micromorph tandem devices.

**FIG. 9.** $V_{oc}$ after light soaking for the hydrogen dilution series of solar cells co-deposited on four substrates with different roughnesses.

**FIG. 10.** TEM image of a 1-μm thick solar cell with an i-layer deposited at the transition from a-Si:H to µc-Si:H. Arrows indicate peaks of the ZnO substrate, above which chains of voids are located. TEM image taken by D. Alexander.
ACKNOWLEDGMENTS

We wish to acknowledge D. Alexander for performing the TEM measurement, M. Carlberg and L. Garcia for taking part of the current-voltage and EQE measurements, S. De Wolf and A. Howling for discussions, T. Matsui from PVTEC (Tsukuba, Japan) for allowing us to use their FTIR and Raman measurement setups, G. Choong from TEL solar (Neuchâtel, Switzerland) for providing us access to their Raman measurement setup, and INDEOtec for the PECVD reactor and technical support.

This work was supported in part by Competence Center Energy and Mobility, and Swisselectric Research (DURSOL project, www.dursol.ch), by the Swiss Federal Office of Energy under Grant SI/500750-01, and by the FP7 Project “Fast Track,” funded by the European Commission under Grant 283501.


21See http://www.indeotec.com for more information about INDEOtec SA (Switzerland).


