Improved amorphous/crystalline silicon interface passivation by hydrogen plasma treatment

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Among high-efficiency devices, silicon heterojunction solar cells have high open-circuit voltages thanks to excellent passivation of the wafer surfaces by thin intrinsic amorphous silicon (a-Si:H) layers deposited by plasma-enhanced chemical vapor deposition. We show a dramatic improvement in passivation when H2 plasma treatments are used during film deposition. Although the bulk of the a-Si:H layers is slightly more disordered after H2 treatment, the hydrogenation of the wafer/film interface is nevertheless improved with as-deposited layers. Employing H2 treatments, 4 cm2 heterojunction solar cells were produced with industry-compatible processes, yielding open-circuit voltages up to 725 mV and aperture area efficiencies up to 21%. © 2011 American Institute of Physics. [doi:10.1063/1.3641899]

Amorphous silicon layers were deposited at 200 °C in two different automated parallel-plate PECVD reactors. The first is a multi-chamber variable frequency reactor by INDEOtec with the following specifications: 15 × 16 cm2 electrode size, 15 mm gap, and radio frequency (RF) excitation (13.56 MHz). The second reactor is a modified version of a large-area industrial KAI-M PlasmaBoxTM reactor8 with the following specifications: 50 × 60 cm2 electrode size, 13 mm gap, very high frequency (VHF) excitation (40.68 MHz). Float zone (FZ) n-type c-Si wafers (4 Ω-cm) were used as substrates, either with (100) or (111) polished surfaces (wafer thickness 300 μm), or with textured surfaces on which (111) faces were revealed (wafer thickness 230 μm). Just before deposition, the native oxide on the wafer surfaces was removed in a hydrofluoric acid solution. After deposition, effective minority carrier lifetimes were measured with a Sinton Consulting WCT-100 quasi-steady-state photoconductance system.9 In addition, a-Si:H films were also characterized ex-situ by spectroscopic ellipsometry and by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Details about the structure and fabrication process of complete heterojunction solar cells are described elsewhere.4

To investigate the effect of H2 treatment on the passivating intrinsic layers, two deposition sequences were tested, as shown in Figure 1. The first consisted of a single step of pure silane plasma; the second consisted of three shorter silane plasma steps (same conditions as for the first deposition type) with an additional short H2 plasma step after each silane step. The durations of the discharges were chosen to deposit a total a-Si:H film thickness of 15 nm in both cases.

Figure 2 gives the effective lifetimes of (100) and (111) c-Si wafers passivated with untreated and treated a-Si:H layers before and during annealing. Annealing reveals important information about the physics of passivation (for example movement of hydrogen in the film and at the interface), and it is also necessary during solar cell fabrication to cure contact metal paste. (111) surfaces are generally easier to passivate, likely because each silicon atom at the (111) surface has only one dangling

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potentially leading to more complex surface hydrogenation.\textsuperscript{11,12} In contrast, there are two dangling bonds per atom on (100) surfaces, allowing for ideal monohydride termination.\textsuperscript{10} By contrast, there are two dangling bonds per atom on (100) surfaces, potentially leading to more complex surface hydrogenation.\textsuperscript{11,12} This may explain the higher lifetimes measured on (111) wafers for both kinds of a-Si:H layers. Hydrogen treatment is clearly beneficial, both before and after annealing: the lifetimes values are roughly doubled on (111) wafers when H\textsubscript{2} treatment is used, the improvement is less pronounced on (100) wafers but still visible. Upon annealing, all samples show a fast initial improvement in passivation, attributed to hydrogen reorganization at the a-Si:H/c-Si interface (migration from the bulk to the interface).\textsuperscript{13,14} Such improvement indicates also that the deposited layers are relatively disordered.\textsuperscript{13} After this large initial improvement, the lifetime obtained with the treated layers shows a rapid saturation followed by a slight decrease after roughly 10 min. On the other hand, samples passivated with untreated layers show constant improvement, at least during the time range explored here. Apparently, the a-Si:H/c-Si interface is well hydrogenated and passivated by as-deposited treated layers, whereas, with untreated layers, hydrogen may diffuse more slowly from the a-Si:H bulk to the interface during annealing. Indeed, Schulze et al.\textsuperscript{14} suggested that the as-deposited interface defect density is determined by the local network structure at the a-Si:H/c-Si interface, while the interface defect density after annealing is determined more by the bulk properties of the film, due to subsequent hydrogen equilibration.\textsuperscript{15} In agreement with this hypothesis, we observed that a single H\textsubscript{2} plasma treatment step (after the first silane plasma) gives similar as-deposited effective lifetimes as three treatment steps. This underlines that the as-deposited a-Si:H/c-Si interface passivation is mainly determined by H\textsubscript{2} treatments in its vicinity.

Infrared spectroscopy of the treated and untreated a-Si:H layers shows significant differences in silicon-hydrogen bonding. Absorbance spectra of layers deposited on (111) polished c-Si wafers are given in Figure 3, in a spectral region where peaks from monohydride (SiH) and higher hydrides (SiH\textsubscript{2}) bonds are present (stretching modes).\textsuperscript{15-18} The spectra of layers deposited on (100) wafers are identical to those on (111) surfaces (not shown), indicating that the crystal orientation has minor influence on the bulk layer properties. The hydrogen content in the layer clearly increases when H\textsubscript{2} treatment is used, since the total area under the SiH and SiH\textsubscript{2} peaks is larger (both layers have the same thickness, verified by ellipsometry).\textsuperscript{16} The ratio of the SiH\textsubscript{2} peak area to the SiH peak area increases with the treatment, indicating that the treated a-Si:H matrix is more disordered and contains more voids than the untreated layer.\textsuperscript{15} This might seem contradictory to the general aim of this study, namely an improvement in a-Si:H material quality by approaching the crystallization transition via H\textsubscript{2} treatment. However, the presence of more hydrogen could be a signature that layers are close to the crystalline transition. It has indeed been shown that the hydrogen content in a-Si:H reaches its maximum value at the transition (obtained by H\textsubscript{2} dilution).\textsuperscript{19} and that disorder in a-Si:H also increases close to the transition.\textsuperscript{20} This increase in disorder might explain the difference in behavior of wafers passivated with treated and untreated a-Si:H layers during annealing (see Figure 2). If the passivation level after prolonged annealing is determined by the bulk properties of the film,\textsuperscript{14} the slight decrease in passivation observed after 10 min with treated layers may reflect their increased disorder. Nevertheless, even if the as-deposited state is not an equilibrium state, the gain in lifetime obtained with H\textsubscript{2} treatments due to the initial good hydrogenation of the interface is really significant. Globally, this treatment-induced improvement is largely dominating an eventual degradation caused by the bulk disorder if
reasonable annealing times are used, as it is the case in the actual device fabrication process.

Increased disorder of the a-Si:H material due to H2 treatment is also observed with spectroscopic ellipsometry measurements. By fitting data with the Tauc-Lorentz model, we found that the broadening parameter $C$, which is related to material disorder, increases slightly from 2 to 2.15 eV when H2 treatment is applied. Hydrogen treatment also increases the bandgap of the a-Si:H material, measured with ellipsometry. The bandgap typically increases from 1.6 to 1.75 eV, but it can be tuned between these two values depending on the treatment duration, as shown in Figure 4. The opening of the bandgap confirms that more hydrogen is incorporated in the a-Si:H layer. Schulze et al. have observed that hydrogen-induced bandgap widening of a-Si:H mainly causes an increase in the valence band offset at the a-Si:H/c-Si interface, which may modify hole transport in devices. Figure 4 also shows that the H2 plasma has an etching effect. By increasing the treatment duration and keeping the deposition time constant, the final film thickness monotonically decreases to zero. Thus, the treatment parameters have to be chosen carefully. Notably, it has been reported that the hydrogen content in a-Si:H might be higher within a few nanometers of the a-Si:H/c-Si interface, leading to a higher bandgap if ultra-thin layers are deposited. In our case, an increase in bandgap with H2 treatment is also observed when the film thickness is kept constant at 10 nm (not shown). Consequently, the effect is linked to the treatment and not to thickness-related causes.

Based on the results presented above, we optimized deposition conditions and treatment parameters to improve the passivation level. Carrier lifetimes up to 11.2 ms and 7.2 ms have been obtained on polished and textured wafers, respectively, with as-deposited a-Si:H layers as thin as 12 nm. On solar cell precursors (textured wafers passivated with $\sim$15 nm $in$ and $ip$ stacks), lifetimes up to 8.3 ms were measured as-deposited, giving a so-called implied open-circuit voltage of 734 mV. The parameters of the best heterojunction solar cells produced with RF and VHF PECVD are given in Table I. The level of passivation is comparable with both PECVD frequencies. Thanks to the excellent passivation obtained using H2 treatments, 21% aperture area efficiency is reached on 4 cm$^2$ cells.

In summary, the quality of intrinsic a-Si:H layers used for c-Si wafer passivation can be modified and improved by H2 plasma treatment during layer growth, without risking epitaxial growth. By going closer to the amorphous-to-crystalline transition, as-deposited H2 treated a-Si:H layers better hydrogenate the wafer/film interface. The bulk of treated films is, however, slightly more disordered due to an increase in the hydrogen content, which might lead to reduced lifetime after excessive annealing. Medium-sized silicon heterojunction solar cells with screen-printed contacts were optimized using this approach, yielding 21% aperture area efficiencies.

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![Figure 4](image)

**Figure 4.** Effect of H2 plasma treatment duration on a-Si:H film thickness and bandgap, measured with spectroscopic ellipsometry. Intrinsic a-Si:H was deposited (RF PECVD) in six steps with H2 treatment after each step. The duration of the deposition steps was the same for all samples; the duration of the H2 treatments was varied.

**Table I.** Illuminated IV parameters (open-circuit voltage, $V_{oc}$; short-circuit current density, $J_{sc}$; and fill factor, FF) of the best 2 $\times$ 2 cm$^2$ heterojunction solar cells obtained with RF and VHF PECVD from textured wafers, measured under standard test conditions (AM-1.5G, 25 °C, in-house measurement).

<table>
<thead>
<tr>
<th>Technique</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF</td>
<td>724</td>
<td>37.0</td>
<td>76.9</td>
<td>20.6</td>
</tr>
<tr>
<td>VHF</td>
<td>725</td>
<td>37.3</td>
<td>77.8</td>
<td>21.0</td>
</tr>
</tbody>
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