

Silicon Oxide Treatment to Promote Crystallinity of p-type Microcrystalline Layers for Silicon Heterojunction Solar Cells

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Abstract. Many silicon heterojunction solar cells tend to suffer modest fill factors due to high series resistance compared to homojunction or high-temperature-passivated-contact-based solar cells. Loss analysis indicates that this limitation lies in the high contact resistance between the wafer and the electrode (through the intrinsic (i) amorphous silicon (*a*-Si:H) passivating layer and amorphous silicon doped layers), mostly originating from the p-type contact. We implement p-type microcrystalline doped layers in heterojunction cells and demonstrate with 2-side contacted devices that a low CO₂ concentration silicon oxide (SiO) plasma treatment on the *a*-Si:H (i) passivating layer allows to reach high crystallinity with thin layers without impeding passivation. The influence of the treatment time and CO₂ concentration on lifetime and nucleation of the microcrystallites is discussed. We then show the potential of such a SiO treatment by comparing, in 2-side contacted devices, amorphous (without SiO treatment) and microcrystalline p-layer, the latter showing efficiency up to 21.5% prior to optimization.

INTRODUCTION

Silicon heterojunction solar cells showed a steady improvement in efficiency in the last 20 years, setting world records for the open-circuit voltage and then efficiency of crystalline-silicon solar cells [1]–[4]. For long, such solar cells have suffered comparatively lower fill-factors (FF) compared to homojunction solar cells [5]. This low FF can to a large extent be attributed to hole extraction from the wafer to the front transparent conductive oxide (TCO), typically indium tin oxide (ITO): The valence-band offset between *a*-Si:H and c-Si, the low doping efficiency of the amorphous silicon (*a*-Si:H) contact layers—especially for p-type doping—and the lower work-function of ITO compared to *a*-Si:H(p) can make transport through the *a*-Si:H layers and recombination with electrons from the ITO problematic [6]–[11]. Thickening the *a*-Si:H(p) layer can mitigate this issue, yet parasitic absorption in this layer makes such approach unattractive to reach high efficiencies [12]. Microcrystalline silicon (μ c-Si:H) layers, grown under slightly different regimes than *a*-Si:H in the same reactors, can be more efficiently doped, and exhibit a lower absorption in the blue-part of the solar spectrum [13]. These layers are therefore highly attractive for improved contacts in heterojunction solar cells. Introducing oxygen was additionally shown to improve their transparency, without affecting the transversal transport through the layer, providing even more transparent p-type contacts [14], [15]. A challenge with the introduction of such layers in crystalline-silicon-based heterojunction solar cells is to nucleate the μ c-Si:H layer on top of the passivating *a*-Si:H layer without impeding its passivation [7], [16], [17].

These considerations apply more strongly to interdigitated back-contacted solar cells (IBC). Achieving a high lifetime is of paramount importance in IBC devices since the bulk should support lateral carrier transport of all charges, relying on photogenerated carriers for the minority carriers (holes in typical n-type wafers). On the other hand, not all the device area is available for extraction of holes since both charge types are extracted from the same side. Finally, to form the recombination junction necessary for tunnel IBC concept [18], highly crystalline μ c-Si:H doped layers are required. The growth of highly crystalline layers on an *a*-Si:H buffer layer is non-trivial and requires strategies to

avoid the propagation of the amorphous network when depositing a layer with a microcrystalline growth regime. These strategies rely on “aggressive” plasma conditions, based either on oxygen-containing plasmas or on very high hydrogen dilution of the precursor. These approaches, successfully applied in thin-film devices for decades [19], can be detrimental to lifetime and alternative strategies are thus required for silicon heterojunction devices [16], [17].

We investigate here various nucleation treatments based on oxygen-containing plasma treatments directly in heterojunction solar cells. Combining such treatment to an optimized deposition process, we demonstrate thin and highly crystalline μc -Si:H(p) layers in silicon heterojunction solar cells without degrading the lifetime provided by intrinsic amorphous silicon layers, allowing efficiency up to 21.5%.

EXPERIMENTAL DETAILS

Solar cells were prepared on 4-inch, n-type float-zone wafers with resistivity around 3 Ohm.cm. Plasma-enhanced chemical vapor deposition (PECVD) was used for all thin-film silicon layers using SiH_4 , H_2 . CO_2 was added for the SiO_x treatment, and tri-methyl boron and phosphine were used as dopant sources. Indium tin oxide (ITO) was deposited by reactive sputtering (through a shadow mask on the front and full-area on the back) and silver was sputtered on the back. An Ag grid was then screen-printed on the 4-cm² solar cells which were then annealed at 210 °C. Minority-carrier lifetime was measured with a Sinton lifetime tester prior to ITO deposition, and current-voltage (IV) was performed on finished devices. Crystallinity was measured by Raman scattering using a UV laser and the resulting spectra were fitted with 3 Gaussian curves centered at 480 cm⁻¹, 510 cm⁻¹ and 520 cm⁻¹ [20].

RESULTS AND DISCUSSION

Introduction of a silicon-oxide treatment

FIGURE 3a shows a sketch of the two-side contacted devices were prepared to illustrate this trade-off for p-type layers. An oxidizing treatment at the a -Si:H surface was introduced. Several conditions of pressure, power, and gas flow ratios were investigated, to enable to promote a fast nucleation of the μc -Si:H(p) layer without introducing a barrier. As can be seen in FIGURE 3b, long treatments tend to deteriorate transport and result in strong barriers, whereas for short treatments (5s for this particular condition), good device performance is maintained.

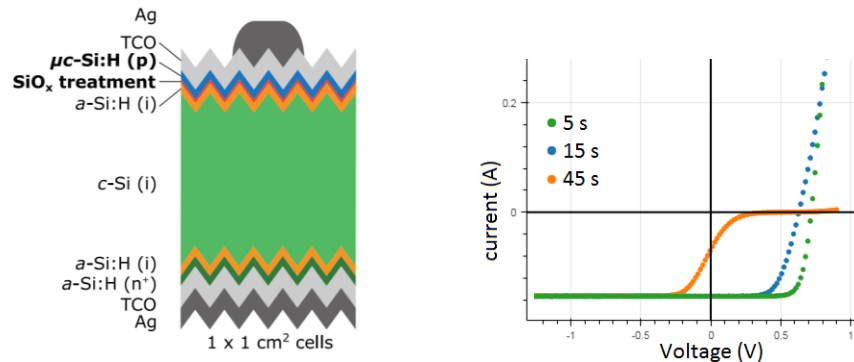


FIGURE 1 (a) Sketch of the devices. (b) IV curves of the devices sketched on the left for different SiO process times showing that long processes are detrimental to hole extraction.

FIGURE 2 shows the influence of the CO_2 concentration during the SiO_x treatment on the lifetime of the wafer at different steps of the PECVD process and on the crystallinity of the μc -Si:H(p) layer grown after this treatment. As seen in FIGURE 2a, similar lifetimes are observed prior to the SiO_x treatment, but a drop of lifetime after the SiO_x pre-treatment is observed in the case of SiO_x treatments with high CO_2 concentration. This degradation is largely reduced for treatments using a low CO_2 concentration in the plasma. Even more relevantly, such condition also results in a higher lifetime after μc -Si:H (p) layer. The crystallinity of the p-layer has been measured by UV-Raman scattering for these different treatment conditions (FIGURE 2b). Similar crystallinity independently of the CO_2 concentration for these treatments could be achieved for treatment times of 5 s to 15 s.

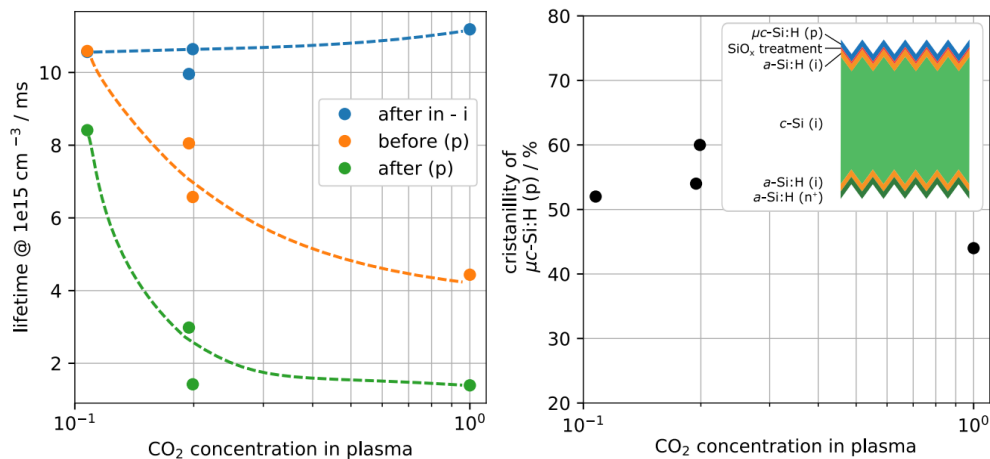


FIGURE 2 (a) Lifetime as function of the CO_2 concentration in the plasma during the SiO_x treatment between the intrinsic $a\text{-Si:H}$ and $\mu\text{c-Si:H (p)}$ layers. (b) Illustration of the crystallinity of the p-layer measured by UV-Raman scattering. The crystallinity remains similar independently from the CO_2 concentration in the plasma.

FIGURE 3 shows the influence of the SiO_x treatment time on the crystallinity of the $\mu\text{c-Si:H(p)}$ layer and on solar cell performance for short times. As seen in FIGURE 3a, though the crystallinity is non-zero for all SiO_x treatments (including no treatment) for the standard p-type layer, this is not the case for the thinner $\mu\text{c-Si:H(p)}$ layer nor for the $\mu\text{c-Si:H(p)}$ layer prepared with lower dilution. Considering the incubative nature of microcrystalline silicon growth, this suggests that a (mostly) amorphous incubation layer is still present for short SiO_x treatment time. However, the longest treatments seem able to prevent or significantly reduce this $a\text{-Si:H}$ incubation phase to grow prior to the phase transition to microcrystalline growth. The longest (15 s) SiO_x pre-treatment yields the highest crystallinity in all cases for this particular regime. FIGURE 3b shows IV curves of 1-cm^2 test cells prepared with these different SiO_x -treatment times and for the case of the standard $\mu\text{c-Si:H(p)}$ layer. Significant series resistance is visible on all except for the longest SiO_x treatment case. We attribute this to the detrimental presence of the amorphous incubation layer, leading to similar transport issues as observed for too thick intrinsic $a\text{-Si:H}$ layers. This also shows that, in this case, 15 s still yields thin-enough layer to allow efficient hole transport. Note that for that particular treatment condition, no layer appears to be deposited during this 15 s treatment based on ellipsometry measurement performed on a flat $a\text{-Si:H}$ -coated glass reference, yet it is expected that too long treatments would lead to deteriorated hole extraction similar to the one observed in FIGURE 3(b).

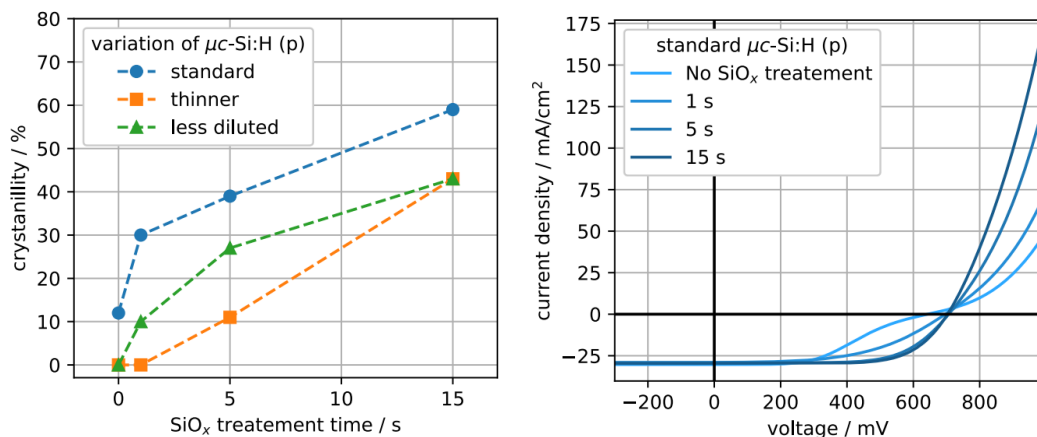


FIGURE 3 (a) Crystallinity of different p-type $\mu\text{c-Si:H}$ layer deposited on an intrinsic $a\text{-Si:H}$ layer subjected to various SiO_x treatment time, measured with UV-Raman; A standard, a twice thinner layer and a layer grown with a lower H_2 dilution are shown. (b) IV curves of 1-cm^2 test solar cells as sketched in Figure 1a for different SiO_x times and a standard $\mu\text{c-Si:H(p)}$ layer, illustrating the beneficial effect of the introduction of a SiO_x treatment.

Solar cell results

FIGURE 4 shows the IV results and typical performance of two-side contacted devices prepared with an optimized SiO treatment. Similar V_{oc} and FF0 (pseudo-FF extracted using the technique discussed in ref. [21]) values are obtained for a reference a -Si:H(p) layer or the μc -Si:H(p) layer, indicating similar passivation property. A 1% loss in FF can be partially attributed to a higher sheet resistance of the co-deposited front TCO. Indeed, $300 \Omega/\text{sq}$ is measured on the μc -Si:H(p) layer instead of $100 \Omega/\text{sq}$ on a -Si:H(p). Such an increase results in $\sim 2\%$ FF loss and its cause is still under investigation. Considering this difference, and noticing that the forward-bias IV curves of both architectures are on the other hand very similar, the high obtained FF indicate an improved hole extraction for the μc -Si:H(p) condition. The $1 \text{ mA}/\text{cm}^2$ loss is explained by the thicker μc -Si:H(p) layer than a -Si:H(p) layer since the former was not optimized for transparency at this stage and is approximately 30-nm-thick, thus the lower efficiency.

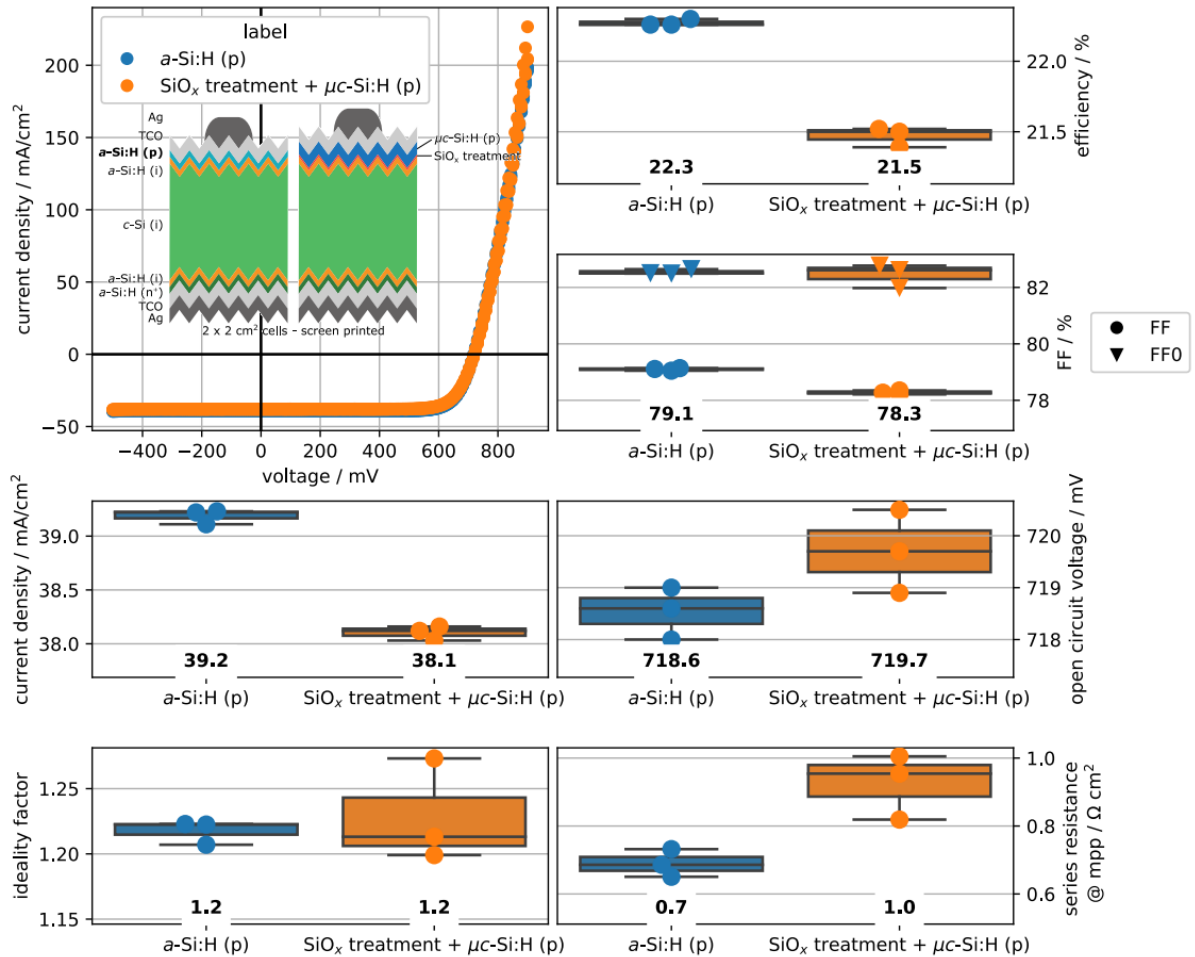


FIGURE 4 IV characteristics and key extracted parameters of silicon heterojunction solar cells using either a standard a -Si:H(p) layer or a μc -Si:H(p) layer with an optimized SiO_x treatment. Similar passivation is obtained as seen from similar V_{oc} and FF0 (corresponding to the pFF), but the efficiency is lower for the μc -Si:H(p) layer case due to lower J_{sc} (thicker layer used) and higher series resistance at maximum power point (R_{mpp}).

CONCLUSION

We show that a well-tuned SiO plasma pre-treatment promotes the fast nucleation of highly crystalline $\mu\text{c-Si:H(p)}$ layers while preserving passivation even after the $\mu\text{c-Si:H(p)}$ layer deposition. Such treatment is implemented in two-side contacted devices leading to solar cells with low series resistance. Further reduction of series resistance is observed by lowering the deposition temperature of the $\mu\text{c-Si:H(p)}$ layer. Compared to our standard $a\text{-Si:H(p)}$ -based solar cells, a slight efficiency drop is observed, with efficiencies up to 21.5%, partly due to non-optimized thickness for use as window layer and higher ITO sheet resistance on the microcrystalline layer compared to the amorphous layer. This SiO pre-treatment has a high potential for application in IBC devices in order to mitigate the lifetime drop after p-layer deposition, promote high crystallinity and hence high FF. By relaxing the requirements in terms of growth regime, such pre-treatment could ease the industrial adoption of the technology, notably by reducing the deposition time and potentially increasing the gas utilization ratio. For a use of the $\mu\text{c-Si:H(p)}$ layer as window layer, optimization of the recipe would be required.

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