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22.5% efficient silicon heterojunction solar cell with molybdenum oxide hole collector

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Substituting the doped amorphous silicon films at the front of silicon heterojunction solar cells with wide-bandgap transition metal oxides can mitigate parasitic light absorption losses. This was recently proven by replacing p-type amorphous silicon with molybdenum oxide films. In this article, we evidence that annealing above 130 °C—often needed for the curing of printed metal contacts—detrimentally impacts hole collection of such devices. We circumvent this issue by using electrodeposited copper front metallization and demonstrate a silicon heterojunction solar cell with molybdenum oxide hole collector, featuring a fill factor value higher than 80% and certified energy conversion efficiency of 22.5%. © 2015 AIP Publishing LLC.

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The current record energy conversion efficiency for crystalline silicon (c-Si) solar cells is 25.6%, which was achieved with silicon heterojunction (SHJ) technology.1 This device featured interdigitated contacts at the back, which offers ultimate freedom in optical optimization at the front but adds processing complexity at the back.2,3 This is in contrast to the most simple “standard” SHJ design, where electron and hole collection is realized at opposite sides of the c-Si wafer.4 In this way, device fabrication only relies on a few well-established processing steps without requiring patterning: Electron and hole collection is achieved by blanket n- and p-type amorphous silicon films [a-Si:H(n)/a-Si:H(p)], respectively. For improved interface passivation—essential to yield high operating voltages—thin intrinsic a-Si:H(i) films are inserted underneath these carrier-collecting films.5,6 The doped a-Si:H layers are capped by transparent conductive oxides (TCO) on both device sides for efficient contact formation, to transport laterally the charge carriers, and to maximize light coupling into the silicon substrate.7,8 Finally, a metal grid is usually printed or electroplated at the front for external current collection.9

In this simple design, for ultimate device performance, the front contact should be broadband transparent. However, due to the relatively narrow bandgap of a-Si:H of ~1.6–1.8 eV and the high defect density within the doped layer, important parasitic light absorption occurs in the ultraviolet and visible range of the solar spectrum.10 Alternative Si-based materials with wider bandgap, such as a-SiO2:H, μc-SiO2:H, or a-SiC2:H, were proposed to overcome this issue.11,12 Unfortunately, proven optical gains for these materials bring along lowered electrical performance due to the increased band offsets at the amorphous/crystalline silicon interface, hindering efficient carrier extraction.13–15

Even more important optical gains may be achieved by using highly transparent transition metal oxides as window layers, provided their work function is appropriate for carrier collection.16,17 Metal oxides, and in particular, sub-stoichiometric molybdenum oxide (MoOx, x < 3), were already investigated as hole collecting materials for organic18–20 and inorganic21–23 thin-film solar cells, as well as for organic light emitting diodes.26–28 For these applications, the metal oxide layer often also protects sensitive underlying layers from sputtering-induced damage during TCO deposition.24,25,29,30 Exploiting their bandgap of ~3 eV, MoOx films were recently also integrated into SHJ devices to replace the a-Si:H(p) layers, resulting in clear optical gains.31 However, the fill factor (FF) of these devices remained below 70%, with increasingly pronounced S-shaped illuminated J–V curves when increasing the MoOx film thickness, indicating a hole collection issue,31 despite its argued appropriate work function.32,33

Importantly, MoOx films are sensitive to air and oxygen exposure, as well as to temperature or plasma treatments, which might impact solar cell performance.34 Motivated by this, we present in this work a detailed investigation of the interactions between MoOx and the layers it shares an interface with the SHJ devices (i.e., the intrinsic a-Si:H buffer layer and the TCO at the front). We demonstrate that with well-engineered processes, efficient hole collection can be obtained with such a contact, enabling measured FF values above 80% in SHJ solar cells.

We processed MoOx-based as well as reference SHJ solar cells [featuring a standard a-Si:H(p) layer] as follows: First, high quality 4 Ω·cm, 230 μm n-type float-zone Si(100) wafers were etched in potassium hydroxide to obtain a random-pyramid surface texture. After chemical cleaning, the wafers were dipped in 5% hydrofluoric acid for 1 min to remove the chemically grown surface oxide. Thin intrinsic a-Si:H films were then deposited by plasma-enhanced...
screen-printed to form the front grid, followed by curing. These films were carried in a N2 purged oven. Film thicknesses were measured using an optical profilometer (Nanofocus EPS2000).37 High-resolution transmission electron microscopy (HR-TEM) was carried out on selected samples using a FEI Osiris instrument. For this, cross-section samples were prepared using mechanical tripod polishing (Allied High Tech Multiprep) followed by low-energy Ar ion milling (Gatan PIPS). Finally, completed solar cells were characterized by light J-V (Wacom solar simulator, Keithley 2601A source meter) and external quantum efficiency (EQE, in-house built setup).

To illustrate the influence of subsequent processing steps on the optical properties of the MoOx layer, Fig. 1(a) shows the optical absorbance of device-relevant MoOx and IO:H/ITO films on glass prior to annealing, either deposited separately or sequentially (IO:H/ITO bilayer sputtered on MoOx film). Absorbance spectra of a-Si:H(p) and of bare AF32 glass substrates are also provided for reference. In the as-deposited state [see panel (a)], as a result of its ~3 eV bandgap, the MoOx spectrum features a cut-off wavelength at 400 nm, while the absorbance in the visible and infrared ranges remains below 2%. The same graph also shows the absorbance of the IO:H/ITO bilayer (deposited at room temperature) used here as highly transparent TCO. Surprisingly, when MoOx is capped with this IO:H/ITO bilayer, the total absorbance is significantly higher than expected from the spectra of the individual layers.25 Increased absorbance of MoOx is known to result from low-temperature annealing in N2 atmosphere [see also Fig. 1(b)], which can be explained by an increase of oxygen vacancies in this material.38,39 In our case, sputtering takes place at a temperature below 50 °C and can therefore not explain these optical changes. Exposing our MoOx films directly to a pure Ar plasma revealed that the increased absorbance is induced both by bombardment with energetic particles and by plasma UV luminescence, causing photochromism of MoOx.40,41

To further investigate the MoOx/ITO interaction and its evolution during annealing, HR-TEM was carried out on mirror-polished c-Si samples, capped with a full a-Si:H(i)/MoOx/IO:H/ITO contact stack. Figures 2(a) and 2(b) show such a stack in its as-deposited and annealed states (25 min at 200 °C in a N2 purged oven), respectively. In either case, an atomically sharp and defect-free c-Si/a-Si:H(i) interface is seen, required for high-quality surface passivation.42 Similarly, the a-Si:H(i)/MoOx interface is clearly delimitated. In contrast, the MoOx/IO:H interface is less sharply resolved, suggesting the presence of a ~1–2 nm-thick intermixing layer induced by the sputtering process [Fig. 2(a)].

Panel (b) indicates that during annealing, the presence of this intermixing layer becomes more pronounced and reaches a thickness of 5–7 nm with the occurrence of epitaxial nano-grains on the IO:H lattice [Fig. 2(b), indicated by the white arrow].

Next, we investigated the impact of the presence of the MoOx layer and the subsequent annealing on the passivation properties of the a-Si:H(i) buffer layer. For this, we evaluated the effective minority carrier lifetime ($\tau_{\text{eff}}$) of the silicon wafer by transient photoconductance measurements (Sinton Instruments, WCT-120), which gives direct information on the surface passivation quality. Figure 3(a) shows $\tau_{\text{eff}}$ (at a carrier injection level of $10^{15}$ cm$^{-2}$) as a function of the annealing temperature. Both passivation samples (with and without MoOx overlayer) increase their $\tau_{\text{eff}}$ within the first minutes of annealing, which is explained by a reorganization of the passivating film’s microstructure.45,46 However, for longer annealing, $\tau_{\text{eff}}$ slightly decays for the MoOx sample. Similar annealing effects were observed in the past when capping a-Si:H(i) buffer layers with p-type a-Si:H films, which was explained by a reorganization of the passivating film’s microstructure.45,46

![FIG. 1. Optical absorbance of MoOx films and IO:H/ITO bilayers deposited separately or sequentially on AF32 glass (a) before and (b) after 200 °C annealing (in N2 for 25 min). Absorbance spectra of a thin a-Si:H(p) film and of bare AF32 glass are given for reference.](image-url)
by Fermi-level induced native defect generation in the passivating films.\textsuperscript{47} Here, the magnitude of this effect remains modest, as seen in Fig. 3(b), where $\tau_{\text{eff}}$ is increased for all injection levels excluding any negative effect on device performance.

Summarizing our findings so far, we conclude that (1) oxygen vacancies are created in the MoO$_x$ film by the TCO deposition process; (2) subsequent annealing may result in the formation of an interlayer between MoO$_x$ and IO:H; (3) the annealing required for the Ag paste curing does not alter markedly the passivation properties of the a-Si:H(i) buffer layer.

To investigate the impact of annealing on device level, we fabricated solar cells featuring either MoO$_x$ or standard a-Si:H(p) hole extraction layers. The cells were metallized by using screen-printing, followed by annealing at the lowest possible temperature to evaporate the solvents contained within the silver paste. This pre-drying is mandatory to obtain a reasonable electrical conductivity and mechanical stability and was carried at 100°C for 25 min (instead of the typically used 200°C for 25 min). Once finished, the cells were subsequently annealed at 130°C, 180°C, and 200°C in steps of 15 min. For the reference cell, Fig. 4(a) confirms that increasing the annealing temperature up to 200°C improves the device performance ($FF$ improves from 75.4% to 77.1%), linked to the improved metal conductivity as well as to improved passivation (seen also in Fig. 3).\textsuperscript{48} In contrast to this, Fig. 4(b) shows that annealing above 130°C dramatically deteriorates the performances of our MoO$_x$-based cell.\textsuperscript{16} The $J-V$ characteristics become S-shaped ($FF$ deteriorates from 76.6% to 69.7%), strongly suggesting the appearance of a hole-blocking barrier. A possible cause for this barrier is the earlier discussed MoO$_x$/TCO interlayer, which thickens with annealing. However, an exhaustive characterization of the interlayer film composition remains necessary to fully establish this view. The occurrence of the S-shaped curves was found to be independent of the annealing ambient (air or N$_2$-purged, data not shown). Hence, processing above 130°C temperature must be avoided to preserve efficient hole collection. In addition, we note that the $J_{SC}$ remains unchanged after annealing as the decreased absorptance in the 650–1200 nm range is counterbalanced by losses in the 400–650 nm range accordingly to Fig. 1.

We now directly compare MoO$_x$-based and reference devices. Figure 5 shows both cell structures featuring identical TCO layers (IO:H/ITO bilayer), but annealed at their respective optimal conditions (namely, 100°C for the MoO$_x$-based cell and 200°C for the reference device). Focusing on the solar-spectrum integrated EQE curves, we see a substantial gain of 0.88 mA cm$^{-2}$ in the 310–610 nm wavelength range for the MoO$_x$-based device. However, this gain is partially lost by parasitic light absorption, caused by the MoO$_x$/TCO interaction, and by the lower optical transparency of non-cured IO:H/ITO films (Fig. 1). At 800 nm, the EQE of the MoO$_x$-based cell is 2% absolute lower than

![FIG. 2. HR-TEM micrographs of the c-Si/a-Si:H(i)/MoO$_x$/IO:H interfaces for (a) an as-deposited sample and (b) after annealing at 200°C in N$_2$ for 25 min. Images are purposely defocused to increase the contrast of the MoO$_x$/IO:H interfacial layer.](image)

![FIG. 3. (a) Minority carrier lifetime at an injection level of $10^{15}$ cm$^{-3}$ as a function of the sample annealing time. (b) Minority carrier lifetime curves in function of the injection level before and after a 32 min annealing.](image)

![FIG. 4. Light $J-V$ characteristics of (a) reference and (b) MoO$_x$-based SHJ solar cells after post-processing annealing at various temperatures. Measurements were taken at room temperature.](image)
MoO$_x$ can be an efficient hole collector, also at standard temperature. In MoO$_x$-based devices, we first deposited a MoO$_x$/IO:H interfacial layer and possibly be the cause of the hole-blocking behavior and FF loss observed when devices are annealed above this temperature. Therefore, by maintaining all processes below this temperature, similar performances as those for a a-Si:H(p) reference SHJ solar cell can be obtained, despite suboptimal material properties. In this respect, specific processes specially designed for low temperatures significantly improve cell performance, such that the conversion efficiency of 22.5% for a 4 cm$^2$ solar cell certified by the Fraunhofer ISE CallLab (Fig. 6). Further simple improvements can be made in the optical design of the cell. For this, the TCOs relying on a thermal treatment for crystallization (as the IO:H/ITO bilayer used in the present study) can be replaced by amorphous TCOs, which do not require any annealing to tune the optical and electrical properties. Furthermore, by replacing IO:H, the sputtering process would not rely on water vapor as a dopant source, which simplifies the process and avoids possible water-MoO$_x$ interactions.

In summary, we showed that when replacing the p-type amorphous silicon film with a MoO$_x$ layer at the front of SHJ solar cells, the properties of the MoO$_x$ layer are strongly impacted by subsequent processing steps. Specifically, sputtering of the TCO leads to increased light absorption, likely due to an increased oxygen vacancy density within the MoO$_x$ film. However, this effect was not found to be detrimental for the electrical cell performance. In addition, processes above 130°C significantly increase the thickness of the MoO$_x$/IO:H interfacial layer and possibly be the cause of the hole-blocking behavior and FF loss observed when devices are annealed above this temperature. Therefore, by maintaining all processes below this temperature, similar performances as those for a a-Si:H(p) reference SHJ solar cell can be obtained, despite suboptimal material properties. In this respect, specific processes especially designed for low temperatures significantly improve cell performance, such that an energy conversion efficiency of 22.5% is demonstrated with copper-plated front metallization. These results therefore demonstrate that metal oxide layers can be used as a hole-blocking layer.

Finally, we discuss how the thermal processing limitation for these devices does not exclude ultimate device performance. In this context, a significant improvement can be achieved by replacing the Ag-printed metallization by Cu electrodeposition, not requiring any thermal treatment. Furthermore, this process reduces substantially the finger width (20 μm, compared to 70–80 μm for screen-printing), reducing optical shadowing from 5%–7% down to 2%–3% while increasing the number of fingers from 9 to 20. To test this in MoO$_x$-based devices, we first deposited a ~30-nm-thick Cu seed layer on the front TCO by thermal evaporation (Leybold Vacuum), which was selectively masked by a photolithographically patterned resist. In the unmasked areas, the Cu was then thickened by electrodeposition at room-temperature, in a home-built system using a Cu sulfate electrolyte. Finally, after photoresist removal, the seed-layer between the fingers was removed in 1 min in a basic Cu etchant at room temperature. Using this modified metallization scheme, the FF of the finished device is significantly increased up to 80.36%, as can be deduced from the illuminated J-V characteristics given in Fig. 6. This is explained by a lower line resistivity in the Cu electrodeposited front-grid compared to the screen-printed cells previously presented, corresponding to a reduction in series resistance from 1.62 to 0.83 Ω-cm$^2$. Moreover, the overall front-grid shadowing is reduced compared to screen-printed cell, resulting in an additional $J_{SC}$ gain.

With these FF and $J_{SC}$ improvements, while maintaining a similar open-circuit voltage ($V_{OC}$), we obtained an energy-conversion efficiency of 22.5% for a 4 cm$^2$ solar cell certified by the Fraunhofer ISE CallLab (Fig. 6). Further simple improvements can be made in the optical design of the cell. For this, the TCOs relying on a thermal treatment for crystallization (as the IO:H/ITO bilayer used in the present study) can be replaced by amorphous TCOs, which do not require any annealing to tune the optical and electrical properties. Furthermore, by replacing IO:H, the sputtering process would not rely on water vapor as a dopant source, which simplifies the process and avoids possible water-MoO$_x$ interactions.
replacement for p-doped amorphous silicon layers in highly efficient SHJ cells, improving optical performance while maintaining excellent passivation and high fill factors.

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