MoO$_x$ and WO$_x$ based hole-selective contacts for wafer-based Si solar cells

Stephanie Essig$^1$, Julie Dréon$^1$, Jérémie Werner$^1$, Philipp López$^1$, Stefaan De Wolf$^2$, Mathieu Boccard$^1$, Christophe Ballif$^1$

$^1$École Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering (IMT), Photovoltaics and Thin-Film Electronics Laboratory, Neuchâtel, Switzerland
$^2$King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

Abstract — Highly-transparent carrier-selective front contacts open a pathway towards entirely dopant free Si solar cells. Hole-selective a-Si:H/MoO$_x$/ITO front contact stacks were already successfully applied in such novel devices. However, for optimum device performance, further improvements are required: We evaluate the use of the high-work-function material WO$_x$ as a replacement for MoO$_x$ in an attempt to reduce optical absorption losses. In addition, we investigate the use of thin hydrogenated SiO$_x$ instead of a-Si:H, and the impact of the residual pressure for MoO$_x$ evaporation.

Index Terms — Silicon heterojunction solar cell, carrier-selective contacts, transition metal oxides

I. INTRODUCTION

The development of dopant-free Si solar cells in which carrier extraction is provided by electron and hole transport layers (ETL and HTL), integrated into passivating contacts, is a promising route to reach efficiencies close to 27% [1]. A typical carrier-selective contact employs a broadband optically transparent material which provides both a chemical passivation of Si surface states and a high (low) work function, inducing in dark and at equilibrium an electrical potential at the Si wafer surface, yielding hole (electron) collection.

A fully doping-free cell with efficiency of 19.4% was realized in ref. [2] by employing a transparent MoO$_x$-based hole-selective contact on the front side and a LiF-based electrowe selective stack on the rear side of an n-type Si wafer. As MoO$_x$ and LiF themselves do not passivate electronic defects at the c-Si surface, thin ~5 nm thick intrinsic hydrogen-rich amorphous silicon (i)a-Si:H interlayers have to be inserted to achieve a high $V_{OC}$. Our present research aims to further optimize the hole-selective front contact, as already used in ref. [2] and [3]. The motivation for this is that the proposed (i)a-Si:H/MoO$_x$/ITO front contact stack comes with an important drawback: parasitic light absorption [3] in both the MoO$_x$, mainly due to transparent conductive oxide (TCO) sputter-induced damage [4], and the ~5 nm thick (i)a-Si:H layer. Furthermore, MoO$_x$ based contact stacks suffer from a fill factor degradation upon annealing at 190°C [5], required for curing of screen printed contacts. This effect could recently be attributed to the release of hydrogen from adjacent layers [6]. In our experiments, we evaluated the possible replacement of MoO$_x$ by WO$_x$ layer. WO$_x$ provides a high work function similar to MoO$_x$ [7, 8] but has a higher transparency both before and after TCO sputter-deposition [4]. Furthermore we tested the impact of the residual base pressure in the evaporation chamber on the performance of solar cells with MoO$_x$-based front contacts and investigated the use of thermal silicon oxide as an alternative passivation layer with higher transparency and improved thermal resilience.

II. EXPERIMENTAL

Float-zone (100) Si wafers with a thickness of 240 μm and resistance of 3 Ωcm (n-type) were textured and cleaned. For solar cell (Fig. 1a) fabrication, 5-nm-thick (i)a-Si:H layers were applied on the front and rear sides by plasma enhanced chemical vapor deposition (PECVD). On the rear side an about 10 nm thick phosphorous doped a-Si:H layer was deposited in the same tool. After loading into an evaporation chamber, an either ~7-nm-thick MoO$_x$ (x<3) or 5-nm-thick WO$_x$ (x<3) layer was deposited on the wafer front side by thermal evaporation using stoichiometric powder (MoO$_3$ or WO$_3$). Then, 2-cm$^2$ sized pads of ITO or IZO/ITO were sputter-deposited on the front side and a full-area ITO/Ag rear contact stack was applied. Front metal grids were deposited by Ag screen-printing and cured 20 minutes at 190 °C.

![Fig. 1. Schematic sketches of (a) our solar cells with MoO$_x$ or WO$_x$ based hole selective front contact, (b) symmetrical structure to test silicon-oxide buffer layers.](image-url)
Symmetrical test structures (Fig. 1b) were fabricated to evaluate the passivation of thin thermal silicon oxide layers (1.5-2.5 nm) as buffer layers underlying the MoO₃. For this, textured 200 μm thick (100) n-type Si wafers (~2 Ωcm) and double side polished (DSP) (100) n-type Si wafers (280 μm, ~3 Ωcm) were cleaned in standard wet-chemical solutions. Thin thermal oxide layers were grown in a Rapid Thermal Processing (RTP) furnace using different peak temperatures \( T_{\text{peak}} \) and oxidation times. Part of the samples were hydrogenated in-situ by a Forming Gas Annealing (FGA) process (30 min, 500 °C). Afterwards, all wafers were loaded in a vacuum chamber to evaporate MoO₃ layers which had an glass thicknesses of about 15 nm. Finally, the minority carrier lifetimes were determined by QSSPC (Quasi Steady State Photo Conductance) measurements.

III. CELLS WITH WOₓ BASED FRONT CONTACTS

Figure 3 shows the JV-curve of our so far best cell with WOₓ-based hole-selective contact and its comparison to a cell with an unoptimized MoOₓ-based contact fabricated in the same evaporation chamber at low base pressures (10⁻⁶ mbar). In both cases, sputtered IZO [9] was used as the front TCO layer, deposited in the same chamber immediately after the MoOₓ or WOₓ thermal evaporation without breaking the vacuum. The cells were characterized after annealing the screen-printed Ag front contact at 190°C. Even though the WOₓ based cell achieves a higher short-circuit current density \( J_{\text{SC}} \), its \( V_{\text{OC}} \) equals only 638 mV (Table 1) compared to 705 mV for the MoOₓ based cell. Both cells suffer from an S-shaped JV-curve close to the \( V_{\text{OC}} \), leading to fill factors of only 70% (WOₓ) and 73% (MoOₓ). Increasing the WOₓ thickness leads to an even stronger S-shape and further reduction in FF (data not shown here). Most likely, the observed low \( V_{\text{OC}} \) and efficiencies of cells with WOₓ based front contact are due to an insufficient band bending provided by our thermally evaporated WOₓ material, as discussed in ref. [10].

![Figure 3](image3.png)

Fig. 3. JV curves of SHJ cells with (i)a-Si:H/MoOₓ/ITO hole-selective front contact. The MoOₓ layers were deposited after evacuating the chamber to a high (~10⁻⁵ mbar) or low (10⁻⁶ mbar) base pressure. MoOₓ layers evaporated in the chamber installed in a N₂ glovebox lead to superior cell performance compared to those deposited in the chamber which was vented in air before each deposition (labelled “H₂O”).

| cell-ID       | \( V_{\text{OC}} \) [mV] | \( J_{\text{SC}} \) [mA/cm²] | FF [%] | eff. [%] |
|---------------|--------------------------|-------------------------------|--------|---------|
| B29w08c4, ~7nm MoO₃ | 705                       | 38.6                          | 72.8   | 19.8    |
| B49w11c3, ~5nm WOₓ   | 638                       | 40.2                          | 70.1   | 18.0    |

IV. IMPACT OF BASE PRESSURE ON MoOₓ BASED CONTACTS

Figure 2 compares JV curves of cells with MoOₓ-based hole-selective front contacts in which the MoOₓ layers were evaporated in vacuum chambers pumped down to different base pressures. We specifically investigated the influence of the water partial pressure by comparing results using a tool equipped with a glovebox and a transfer chamber as a water-free deposition tool (labelled \( N_2 \)), and a tool opened to air before pumping down (thus with most residual pressure being water vapor, labelled as H₂O). Pumping times were adjusted in both tools to reach a base pressure around 10⁻⁵ mbar (labelled high p) or 10⁻⁶ mbar (labelled low p). ITO was then sputter-deposited on all samples, a silver grid was screen printed, and samples were cured at a low temperature of 130 °C. All JV curves show very similar \( V_{\text{OC}} \) and \( J_{\text{SC}} \). A slight S-shape is observed in all cases, yet much more pronounced for the sample prepared with a high base pressure in the tool vented to atmosphere (high p H₂O). This suggests that residual water during evaporation can impact negatively the performance of MoOₓ-based devices.
Figure 4 compares the minority carrier lifetimes of symmetrical test structures with different buffer layers underneath the thermally evaporated MoOx. The investigated silicon oxide layers were generated by two different recipes leading to oxide thicknesses of 2.0 nm and 2.4 nm, as summarized in Table 2. The thin thermal oxide layers result in higher lifetimes than achieved with a reference sample that was HF-dipped prior to the MoOx deposition (no buffer). However their lifetimes of 100 µs to 170 µs at an injection level of 1.10^15 cm^3 are one order of magnitude lower than achieved with an (i)a-Si:H buffer layer (~6 ms). Our data indicate that the surface passivation increases with increasing oxide thickness and hydrogenation. Hydrogenation of the oxide layer 2 (DSP wafer) prior to MoOx deposition resulted in a higher lifetime (Fig. 4) which translates into an increase in implied V_OC (iV_OC) from 603 mV to 621 mV. The same effect was observed on textured (TXT) wafers which achieved an iV_OC up to 650 mV (hydrogenated oxide 2, Fig. 4).

Further analysis is necessary to investigate the carrier transport in SiOx/MoOx/TCO contact stacks and to achieve higher passivation levels comparable to (i)a-Si:H. We expect that there will be a tradeoff between passivation and series resistance for the oxide layer thickness when applied in a real solar cell device.

Table 2. Parameters used for the different rapid thermal oxidations. The oxide thicknesses were determined by spectral ellipsometry on reference DSP Si (100) wafers.

| Oxide recipe | T_peak [°C] | oxidation time [s] | Oxide thickness measured on DSP [nm] |
|--------------|-------------|--------------------|-------------------------------------|
| Oxide 1      | 700         | 90                 | 2.0                                 |
| Oxide 2      | 750         | 90                 | 2.4                                 |

![Fig. 4. Carrier lifetime versus minority carrier density (MCD) of symmetrical test structures (Fig 1b) with different buffer layers as described in the text.](image)

V. CONCLUSION AND OUTLOOK

Our experimental results show that both MoOx and WOx can be used in hole-selective contacts. However, so far WOx-based hole-selective contacts resulted in lower V_OC. The performance of a-Si:H/MoOx/TCO hole-selective contact stacks depends critically on the base pressure and residual water vapor in the deposition chamber. Symmetrical test structures with stacks of 2.4 nm thick hydrogenated SiOx layers and MoOx resulted in iV_OC of 650 mV. Further investigation is required to evaluate its applicability in a real device and its optimal properties for best performance.

ACKNOWLEDGEMENTS

The authors would like to thank Raphaël Monnard and Guillaume Charitat from EPFL and Nicolas Badel from CSEM for work performed in the context of this publication. S. Essig holds a Marie Skłodowska-Curie Individual Fellowship from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No: 706744, action acronym: COLIBRI). Part of this work was supported by the European Union’s Horizon 2020 Programme for research, technological development and demonstration Grant Agreements no. 727529 (project DISC).
REFERENCES

1. Battaglia, C., A. Cuevas, and S. De Wolf, High-efficiency crystalline silicon solar cells: status and perspectives. Energy & Environmental Science, 2016. 9(5): p. 1552-1576.
2. Bullock, J., et al., Efficient silicon solar cells with dopant-free asymmetric heterocontacts. Nature Energy, 2016. 1: p. 15031.
3. Geissbühler, J., et al., 22.5% efficient silicon heterojunction solar cell with molybdenum oxide hole collector. Applied Physics Letters, 2015. 107(8): p. 081601.
4. Werner, J., et al., Parasitic Absorption Reduction in Metal Oxide-Based Transparent Electrodes: Application in Perovskite Solar Cells. ACS Applied Materials & Interfaces, 2016. 8(27): p. 17260-17267.
5. Geissbühler, J., et al., Silicon Heterojunction Solar Cells With Copper-Plated Grid Electrodes: Status and Comparison With Silver Thick-Film Techniques. IEEE Journal of Photovoltaics, 2014. 4(4): p. 1055-1062.
6. Essig, S., et al., MoO$_3$-based hole-selective contacts for Si photovoltaics: hydrogen-rich layers as fill-factor killers. submitted.
7. Gerling, L.G., et al., Transition metal oxides as hole-selective contacts in silicon heterojunctions solar cells. Solar Energy Materials and Solar Cells, 2016. 145, Part 2: p. 109-115.
8. Bivour, M., et al., Molybdenum and tungsten oxide: High work function wide band gap contact materials for hole selective contacts of silicon solar cells. Solar Energy Materials and Solar Cells, 2015. 142: p. 34-41.
9. Morales-Masis, M., et al., Low-Temperature High-Mobility Amorphous IZO for Silicon Heterojunction Solar Cells. IEEE Journal of Photovoltaics, 2015. 5(5): p. 1340-1347.
10. Mews, M. et al., Oxygen vacancies in tungsten oxide and their influence on tungsten oxide/silicon heterojunction solar cells. Solar Energy Materials & Solar Cells 158, pp. 77–83 (2016).