

Hole Selective MoO_x Contact for Silicon Heterojunction Solar Cells

Corsin Battaglia^{1,2}, Silvia Martín de Nicolás³, Stefaan de Wolf³, Xingtian Yin^{1,2}, Maxwell Zheng^{1,2},
Christophe Ballif³ and Ali Javey^{1,2}

¹Electrical Engineering and Computer Sciences Department, University of California, Berkeley, CA 94720

²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

³Photovoltaics and Thin Film Electronics Laboratory, Ecole Polytechnique Fédérale de Lausanne, 2000
Neuchâtel, Switzerland

Abstract — Efficient carrier selective contacts and excellent surface passivation are essential for solar cells to reach high power conversion efficiencies. Exploring MoO_x as a dopant-free, hole-selective contact in combination with an intrinsic hydrogenated amorphous silicon passivation layer between the oxide and the crystalline silicon absorber, we demonstrate a silicon hetero-junction solar cell with a high open-circuit voltage of 711 mV and a power conversion efficiency of 18.8%. Compared to the traditional p-type hydrogenated amorphous silicon emitter of a traditional silicon heterojunction solar cell, we observe a substantial gain in photocurrent of 1.9 mA/cm² for MoO_x due to its wide band gap of 3.3 eV. Our results on MoO_x have important implications for other combinations of transition metal oxides and photovoltaic absorber materials.

Index Terms — heterojunction solar cells, high workfunction, molybdenum trioxide, passivation, photovoltaics, silicon, selective contact, x-ray photoelectron spectroscopy

I. INTRODUCTION

A selective contact, which extracts holes and blocks electrons on one side of a light absorbing semiconductor, and a complementary contact, which extracts electrons and blocks holes on the other side, are fundamental to the operation of a solar cell [1]. Low carrier recombination at the contacts is crucial to reach high power conversion efficiencies. Traditional silicon solar cells achieve carrier selectivity through the formation of diffused homojunctions which are subsequently passivated with silicon nitride. On the other hand, silicon heterojunction solar cells, with demonstrated efficiencies of up to 24.7% [2-3], rely on passivation provided by intrinsic hydrogenated amorphous silicon (a-Si:H) which is deposited first, followed by a p-type or n-type doped carrier-selective a-Si:H contact for hole or electron extraction respectively.

Here we present a radically different selective contact scheme for silicon heterojunction solar cells making use of transition metal oxides as carrier selective contacts [4]. In particular we investigate the use of substoichiometric molybdenum oxide (MoO_x, x<3) as hole selective contact for silicon heterojunction solar cells and demonstrate a high open-circuit voltage (V_{oc}) of 711 mV and a gain in short-circuit

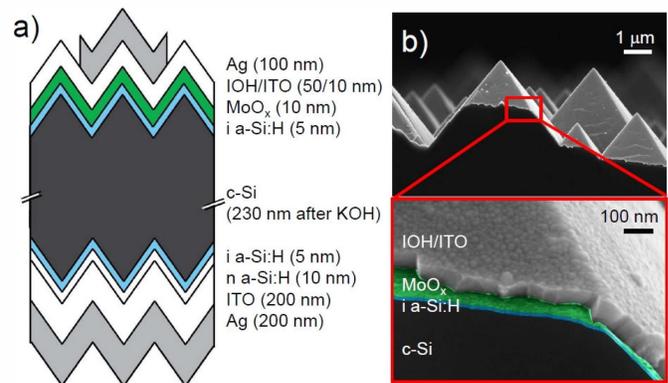


Fig. 1. (a) Schematics of the MoO_x/n-Si heterojunction solar cell structure with (b) false-colored cross section imaged by scanning electron microscopy. Pyramids in (a) are not drawn to scale and are not necessarily commensurate on front and back side (from Ref. [4])

current density (J_{sc}) of 1.9 mA/cm² with respect to a traditional p-type a-Si:H emitter.

II. EXPERIMENT

Fig. 1a shows a schematics of the investigated cell structure, where the p-type a-Si:H emitter of a traditional silicon heterojunction solar cell was replaced by a 10 nm thick thermally evaporated MoO_x layer. Cleaved cross sections of the device imaged by scanning electron microscopy (SEM) are shown in Fig. 1b. The pyramidal surface texture, obtained by alkaline wet etching of the (100)-oriented n-type crystalline silicon wafer (230 μm after etching), serves to maximize light absorption. The a-Si:H layers were deposited by plasma-enhanced chemical vapor deposition, while the indium oxide transparent electrodes and silver backcontact were deposited by sputtering. The silver finger grid on the front side was screen printed. The transparent conductive indium oxide is necessary, as the conductivity of both MoO_x and p-type a-Si:H are insufficient to guarantee carrier transport to the silver fingers. Details concerning layer deposition, cell fabrication, processing and characterization are given in Ref. [4].

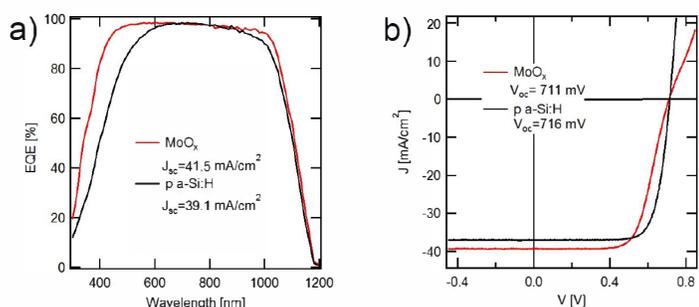


Fig. 2. Comparison of (a) EQE and (b) J(V) curve between silicon heterojunction solar cell with MoO_x and p-type a-Si:H hole contact (from Ref. [4]).

III. RESULTS

External quantum efficiency (EQE) and current voltage characteristic (J(V)) measured under standard test conditions (1000 W/m², air mass 1.5g spectrum, 25° C) of a silicon heterojunction solar cells with MoO_x hole contact are compared in Fig. 2a and b to a reference cell with standard p-type a-Si:H emitter. In the EQE in Fig. 2a, a strong enhancement in the short wavelength region below 700 nm is observed accounting for a substantial increase in J_{sc} by 1.9 mA/cm². This enhancement can be explained with the wider band gap of MoO_x of 3.3 eV compared to the 1.7-1.8 eV for p-type a-Si:H resulting in reduced parasitic absorption in the blue and visible part of the solar spectrum. In fact, the low blue response of traditional silicon heterojunction cells represents an important performance limitation. Efforts directed toward improving the blue response have included replacing a-Si:H by amorphous silicon oxide (a-SiO_x:H) and amorphous silicon carbide (a-SiC_x:H) [7-10], but current gains remained modest (0.4 mA/cm² in Ref. [7]). The 1.9 mA/cm² improvement observed for MoO_x is close to the maximum possible current enhancement of 2.1 mA/cm² assessed through modeling in Ref. [5].

A slight increase in EQE accounting for an increase in short-circuit current of 0.5 mA/cm² is also observed for wavelengths longer than 700 nm. This can be explained by the reduced free carrier absorption in the hydrogen doped indium oxide electrode when compared to standard indium tin oxide and has been discussed in detail in Ref. [9].

From the J(V) characteristics in Fig. 2b, we extract a V_{oc} of 711 mV for the cell with MoO_x contact. This value is close to the 716 mV obtained for the p-type a-Si:H emitter. This indicates that passivation is hardly affected by the MoO_x deposition. J_{sc} values of 39.4 mA/cm² for the MoO_x cell vs 37.1 mA/cm² for the reference cell are consistent with the currents extracted from EQE given in Fig. 3a correcting for 5% shading of the Ag grid not present during EQE measurements.

The J(V) characteristics of the MoO_x cell exhibits a slight “s-shape” reducing its fill factor (FF) to 67.2%. This is markedly lower than the FF of the reference cell with a FF of

75.9%. This affects the overall power conversion efficiency, which remains at present lower for the MoO_x cell with 18.8% compared to the reference cell with 20.2%. The s-shaped curve straightens out a higher temperature (measurements not shown here) leading to an increase of FF with temperature [4]. This behavior is in contrast to the behavior of the reference cell, whose FF decreases with temperature, resulting in the efficiencies of the two cells to converge at an operating temperature of 70° C. A similar behavior has been observed for cells with a-SiO_x emitters in Ref. [5] and has been shown through modeling to be due to non-favorable band offsets.

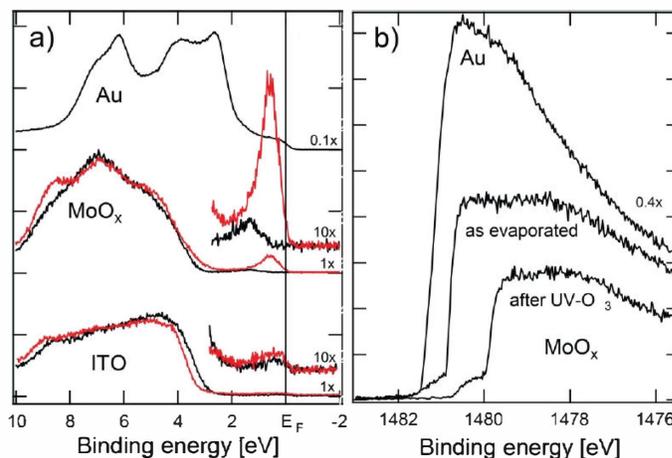


FIG. 3. (a) Comparison of density of states at the Fermi level for ITO, MoO_x, and Au reference. The as-deposited MoO_x film is shown in black and the N₂ annealed film, in red. ITO films with 10²¹ and 10²⁰ cm⁻³ electrons are shown in red and black respectively. (b) Secondary electron cutoff for MoO_x and Au reference. The intensity at the high binding energy side of the steep cutoff is due to an analyzer specific artifact. The evaporated MoO_x film was exposed to UV-ozone (UV-O₃) to increase the workfunction by removal of organic surface adsorbates. (from Ref. [10]).

To better understand the band alignment of MoO_x with respect to a-Si:H we performed x-ray photoelectron spectroscopy using a monochromated Al K_α x-ray source with photon energy 1486.7 eV. Fig. 3a shows valence band spectra of as deposited and annealed MoO_x. For comparison the valence spectra of a gold reference with a clear Fermi step at zero binding energy and degenerately doped ITO films with two different carrier densities are also shown. While MoO_x is commonly considered to be a semiconductor with a band gap of 3.3 eV, Fig. 3a shows that MoO_x may be considered to behave as a high workfunction metal with a low density of states at the Fermi level originating from the tail of an oxygen vacancy derived defect band located inside the band gap at 2 eV above the valence band maximum [10]. Fig. 3b shows the secondary electron cut-off of the photoelectron spectrum from

which we extract the workfunction by subtracting the cut-off energy from the photon energy (the spectra are corrected for an externally applied bias of -9.87 V on the sample, which accelerates photoelectrons away from the sample into the detector. This yields a workfunction of 5.1 eV for the gold reference in agreement with literature [11]. MoO_x transferred in ambient air into the photoemission chamber yields a workfunction of 5.7 eV which further increases to 6.6 eV upon in-situ ozone exposure which cleans the MoO_x surface from adsorbates including adventitious carbon, water and oxygen related species [12].

While a workfunction of 6.6 eV should be high enough to allow hole extraction from a-Si:H without the formation of s-shaped J(V) curves, the high sensitivity of the workfunction of MoO_x to ambient gas exposure requires that MoO_x is capped by ITO without breaking vacuum. This was not possible with the experimental setup used here, but is in principle straightforward to implement. Alternatively to thermal evaporation, MoO_x could be deposited by sputtering, which potentially provides better control over the oxygen-vacancies and consequently the defect state density inside the band gap.

IV. CONCLUSIONS

We introduced MoO_x as hole selective contact in combination with a a-Si:H passivation layer for silicon heterojunction solar cells delivering a respectable efficiency of 18.8% for such an exploratory approach. A V_{oc} comparable to state-of-the-art silicon heterojunction solar cells and a substantial current gain in the short-wavelength region were demonstrated. We further highlighted potential routes to improve efficiency further by eliminating the influence of ambient gases on the workfunction of MoO_x . With a high workfunction exceeding those of all elemental metals [13], MoO_x also opens important opportunities for contacting holes in low lying valence bands of other inorganic semiconductors.

REFERENCES

[1] P. Würfel, "Physics of Solar Cells: From Principles to New Concepts", Wiley, Weinheim, Germany (2005)

[2] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, E. D. Dunlop, "Solar cell efficiency tables (version 42)", *Prog. Photovolt: Res. Appl.* 21, 827-837 (2013)

[3] M. Taguchi, A. Yano, S. Tohoda, K. Matsuyama, Y. Nakamura, T. Nishiwaki, K. Fujita, E. Maruyama, "24.7% Record Efficiency HIT Solar Cell on Thin Silicon Wafer", *IEEE J. Photovolt.*, 4, 96-99 (2013)

[4] C. Battaglia S. Martín de Nicolás, S. De Wolf, X. Yin, M. Zheng, C. Ballif, A. Javey, "Silicon heterojunction solar cell with passivated hole selective MoO_x contact", *Appl. Phys. Lett.* 104, 113902 (2014)

[5] J. P. Seif, A. Descoedres, M. Filipic, F. Smole, M. Topic, Z. C. Holman, S. De Wolf, C. Ballif, "Amorphous silicon oxide window layer for high-efficiency silicon heterojunction solar cells", *J. Appl. Phys.* 115, 024502 (2014)

[6] H. Fujiwara, T. Kaneko, M. Kondo, "Application of hydrogenated amorphous silicon oxide layers to c-Si heterojunction solar cells", *Appl. Phys. Lett.* 91, 133508 (2007)

[7] D. Pysch, M. Bivour, M. Hermle, and S. W. Glunz, "Amorphous silicon carbide heterojunction solar cells on p-type substrates", *Thin Solid Films* 519, 2550-2554 (2011)

[8] T. Mueller, S. Schwertheim, M. Scherff, W. R. Fahrner, "High quality passivation for heterojunction solar cells by hydrogenated amorphous silicon suboxide films", *Appl. Phys. Lett.* 92, 033504 (2008)

[9] Z. C. Holman, A. Descoedres, L. Barraud, F. Zicarelli Fernandez, J. P. Seif, S. De Wolf, C. Ballif, "Current Losses at the Front of Silicon Heterojunction Solar Cells", *IEEE J. Photovolt.* 2, 7-15 (2012)

[10] L. Barraud, Z. C. Holman, N. Badel, P. Reiss, A. Descoedres, C. Battaglia, S. De Wolf and Ballif, "Hydrogen-doped indium oxide/indium tin oxide bilayers for high-efficiency silicon heterojunction solar cells", *Sol. Energy Mat. & Sol. Cells* 115, 151-156 (2013)

[11] C. Battaglia, X. Yin, M. Zheng, I. D. Sharp, T. Chen, S. McDonnell, A. Azcatl, C. Carraro, B. Ma, R. Maboudian, R. Wallace and A. Javey, "Hole selective MoO_x contact for silicon solar cells", *Nano Lett.* 14, 967 (2014)

[12] Y. Baer, "The natural energy scale for XPS spectra of metals", *Sol. State. Comm.* 19, 669-671 (1976)

[13] T. L. Barr and S. Seal, "Nature of the use of adventitious carbon as binding energy standard", *J. Vac. Sci. Technol. A* 13, 1239 (1995)

[13] H. B. Michaelson, "The workfunction of the elements and its periodicity", *J. Appl. Phys.* 48, 4729 (1977)