Sputter-deposited WO$_x$ and MoO$_x$ for hole selective contacts

Martin Bivour$^{a,*}$#, Florian Zähringer$^{a,1}$, Paul Ndione$^{a,b}$, Martin Hermle$^a$

$^a$Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstrasse 2, 79110 Freiburg, Germany,
$^b$National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA

Abstract

Reactive sputter deposited tungsten and molybdenum oxide (WO$_x$, MoO$_x$) thin films are tested for their ability to form a hole selective contact for Si wafer based solar cells. A characterization approach based on analyzing the band bending induced in the c-Si absorber and the external and implied open-circuit voltage of test structures was used. It is shown that the oxygen partial pressure allows to tailor the selectivity to some extent and that a direct correlation between induced band bending and hole selectivity exists. Although the selectivity of the sputtered films is inferior to the reference films deposited by thermal evaporation, these results demonstrate a good starting point for further optimizations of sputtered WO$_x$ and MoO$_x$ towards higher work functions to improve the hole selectivity.

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Peer review by the scientific conference committee of SiliconPV 2017 under responsibility of PSE AG.

Keywords: Metal oxide; work function; induced junction; sputtering

1. Introduction

Proper engineering of metal oxide properties is fundamental to the optical and electrical characteristics of many devices. For a high transparency and sufficient lateral transport, a low carrier density and high mobility are essential. Indium-based oxides are materials of choice for such transparent and conductive oxides (TCOs). With respect to the formation of carrier selective contacts, amongst others, a high (low) work function of the TCO close to the valence (conduction) band of the absorber is needed to form a hole (electron) selective contact. The basic applicability of

* Corresponding author. Tel.: +49 761/4588-5586.
E-mail address: Martin.Bivour@ise.fraunhofer.de
# M. Bivour and F. Zähringer contributed equally to this work.
high work function n-type transition metal oxides like e.g. MoO$_x$ and WO$_x$ for this purpose was proven for organic electronics, silicon thin film absorbers [1], [2], [3] and more recently for c-Si wafer based solar cells [4], [5], [6], [7]. These films are typically deposited by thermal evaporation which offers the benefit of a “soft” deposition and material properties enabling good selectivity. However, for further improvements and better understanding of the relevant material properties, more control over the metal oxide properties like defect characteristics, stoichiometry, work function and charges which are responsible for the induced c-Si junction, efficient tunneling transports and the conductivity are needed. Reactive sputtering is one alternative deposition technique which should be of more industrial relevance and has proven useful to tune the properties of metal oxides by varying the deposition condition. For instance, it was shown for the n-type TCOs that the decrease (increase) of the bulk carrier density results in an increase (decrease) of their surface work function since the Fermi-level moves towards the valence (conduction) band [8]. So far, only limited investigations on sputtered MoO$_x$ [9] and WO$_x$ [10] for silicon solar cells have been carried out. In this sense, the basic applicability and tunability of sputtered MoO$_x$ and WO$_x$ and of a relatively simple and meaningful characterization approach is investigated here. Basically, for reactive sputtering from a metal target the addition of oxygen in the process gas will results in a transition from metallic to oxidic films. For these n-type films this could be accompanied by a design trade-off between increasing work function and decreasing carrier density / conductivity. However, especially for highly resistive films featuring a large screening length, it can be expected that their Fermi-level and hence actual properties are easily modify the by the work function of the adjacent layers, i.e. the low work function ITO capping. Another possible influence for films sputtered at highly oxygen containing plasma conditions might be the oxidation of the a-Si:H buffer during the film grows, hampering the hole extraction in the final device. The latter was speculated to dominate over the work function improvement for the ITO / a-Si:H contact in Ref. [11] for films deposited at high oxygen contents.

2. Experimental details

The influence of the MoO$_x$ and WO$_x$ deposition conditions on the hole contact properties was investigated with simple small area solar cell like test structures shown in Fig. 1a. An a-Si:H(i) buffer is used for good surface passivation and the MoO$_x$ and WO$_x$ thickness is kept between about 10 and 15 nm.
2.1. Sputtering

To tune the stoichiometry of the MoOx and WOx films and the sputter damage reactive sputtering in the DC mode from a molybdenum or tungsten target with a variable O₂ content (OC) in the sputtering gas [OC = O₂/(O₂+Ar)] is applied. While other parameters like the metal oxide thickness, power, pressure, deposition temperature and optical film properties have also been investigated, we will concentrate on the OC and the post-deposition annealing temperature (hot plate annealing) here. Sputtering was performed at 120 W from a 10 cm wide target at a pressure of about 100×10⁻³ mbar and at a fixed Ar flow of 500 sccm. Further details will be published in an upcoming publication. nIn precursors featured good surface passivation before deposition of the TMO, quantified by an implied Vₜₐᵢₖ of above 700 mV.

2.2. Characterization

To take into account that the electrical characteristic and electrical losses of such non-optimized contacts might not obey the classical diode law an characterization approach adapted from Ref. [12] is used. It is based on the relatively simple current-less measurements of the induced c-Si equilibrium band bending (Vₑₒₒ in Fig. 1b), the external Vₑₒₙ and the implied Vₑₒₙ (iVₑₒₙ) of simple small area solar cell precursors. It allows identifying weather the characteristic of the contact is not only determined by the standard recombination and ohmic shunt and ohmic transport losses but also by an insufficient selectivity, i.e. a “non-ideal” rectifying behavior. We have found it useful to use ΔVₑₒₙ as a figure of merit for the contact’s selectivity and a selection criterion for further investigations, e.g. to justify investigations on solar cell level. Vₑₒₒ is measured by the surface photo-voltage technique [15] and gives valuable information on the inversion of the c-Si surface and the corresponding induced c-Si junction which is of major importance for the selectivity of such induced junctions [16], [11]. Thus, Vₑₒₒ provides indirect information on the effective work function [17] which is determined by the MoOₓ bulk and the interfacial MoOₓ and a-Si:H properties causing the inversion and hence the asymmetric hole / electron conductivity (i.e. low-injection conditions) needed for a negligible gradient in the Fermi-level of the contacts majority carriers during operation [14], [18], [12].

3. Results and discussion

3.1. MoOₓ

Comparing the results between sputtered (balls) and thermally evaporated MoOₓ films (stars) Fig. 2a reveals that a significant sputter damage is observed in the as deposited stated (black). Similar to the sputtering of ITO [19], subsequent annealing allows to partly cure this damage and good iVₑₒₙ up to 705 mV can be reached for OC > 0 %. Fig. 2b shows that external Vₑₒₙ of the sputtered films is limited to below 620 mV which means that ΔVₑₒₙ = iVₑₒₙ - Vₑₒₙ >> 0 (Fig. 2c). Accordingly, the performance of all sputtered contacts is limited by an insufficient ability of the MoOₓ films to extract the excess holes from the absorber, i.e. and insufficient hole selectivity. While surface passivation benefits from annealing up to 240°C (blue), the selectivity (ΔVₑₒₙ) is only improved for the 150°C annealing (red) and decreased for higher temperatures. This interplay leads to the fact that the highest external Vₑₒₙ is reached for annealing at 180°C (green). The optimum OC is close to 1 % which is the minimum value that could be chosen for the experimental setup. The results from Fig. 2c are plotted as a function of the induced c-Si band bending in Fig. 2d. The linear dependence reveals that selectivity is governed by the inversion of the c-Si absorber and built-in potential [13], [11] which mainly results from the effective work function and the charges of the MoOₓ films. It should be noted that ideally a linear dependence with a slope of unity is expected from device simulations [11], which is in reasonable agreement with the experimental value of 0.77. The linear dependence is explained by the fact that Vₑₒₒ defines the asymmetry of the hole / electron density of the induced (p/n) junction during equilibrium. Hence, a certain value of Vₑₒₒ (basically Vₑₒₒ > Vₑₓₑₜₐᵢₖ) is needed to maintain this asymmetry (i.e. low-
injection conditions) also for operation when the increase of the hole and electron density by the same amount will reduced this asymmetry. In other words, the contact region must not operate in high-injection. This ensures ideal selectivity and voltage extraction from the absorber [11] and hence the basic applicability of the classical diode law.

The linear dependence of $\Delta V_{oc}$ on $V_{bb}$ as shown in Fig. 2d or of the external $V_{oc}$ has been observed experimentally for other contacts limited by non-ideal selectivity based on atomic layer deposited MoO$_x$ [20], evaporated WO$_x$ [21] and metal films featuring different work functions [22], [10]. Accordingly, a more efficient engineering of the sputtered MoO$_x$ films towards higher work functions is needed to approach the higher induced c-Si band bending and hence better selectivity of the evaporated films. For the latter, at least in the as deposited state, the external $V_{oc}$ is limited by surface passivation ($iV_{oc}$) and not $\Delta V_{oc}$.

### 3.2. WO$_x$

For good surface passivation a sufficient annealing and OC > 0 % are also needed for the sputtered WO$_x$ contacts (Fig. 3a). Similar to MoO$_x$ the external $V_{oc}$ is clearly limited by a poor selectivity and inferior the control samples featuring the evaporated films. While the optimum annealing temperature is shifted to higher temperatures (240 vs. 150°C) the overall level of the $V_{oc}$ and $\Delta V_{oc}$ is even worse compared to the sputtered MoO$_x$ contacts. The optimum OC seems slightly higher and is near 3 %. The dependence of $\Delta V_{oc}$ on $V_{bb}$ in Fig. 3d seems to be different to the MoO$_x$ contact but it can be seen that the improved selectivity with annealing at 240°C is linked to an improved induced c-Si band bending.
4. Summary

Some aspects for the optimization of passivating and carrier selective induced junctions based on sputtered MoO$_x$ or WO$_x$ thin films were addressed. A clear correlation between the induced c-Si band bending and the hole selectivity was observed and the basic applicability of the proposed characterization approach was proven. It was shown that reactive DC sputtering is in principle suited to tailor the metal oxide properties and hole selectivity. Although the selectivity of the sputtered films is inferior to the reference films deposited by thermal evaporation, these results demonstrate a good starting point for further optimizations of sputtered WO$_x$ and MoO$_x$. Especially for MoO$_x$ higher work functions are needed to improve the hole selectivity. Basically, structural and chemical investigations comparing the better performing thermally evaporated contacts with the sputtered ones would be helpful to improve the understanding.

Acknowledgements

The colleagues at ISE are acknowledged for the experimental / technical assistance. This work was funded by the German Federal Ministry for Economic Affairs and Energy under contract number 0324141 “SELEKTIV”.

Fig. 3: Results from the variation of the oxygen content in the sputtering gas during sputtering from a W target for different post-deposition annealing temperatures. It should be noted that, unlike Fig. 2d, $V_{bb}$ in Fig. 3d was not measured on the same samples as those used to determine $\Delta V_{bb}$. A more simple WO$_x$ / c-Si(n) configuration was used instead. Accordingly, a direct comparison between Fig. 2d and 3d might be misleading since a possible influence of the buffer and the ITO electrode is absent.
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Fig. 3: Results from the variation of the oxygen content in the sputtering gas during sputtering from a W target for different post-deposition

Acknowledgements


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