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Sputter-deposited WO_x and MoO_x for hole selective contacts

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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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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

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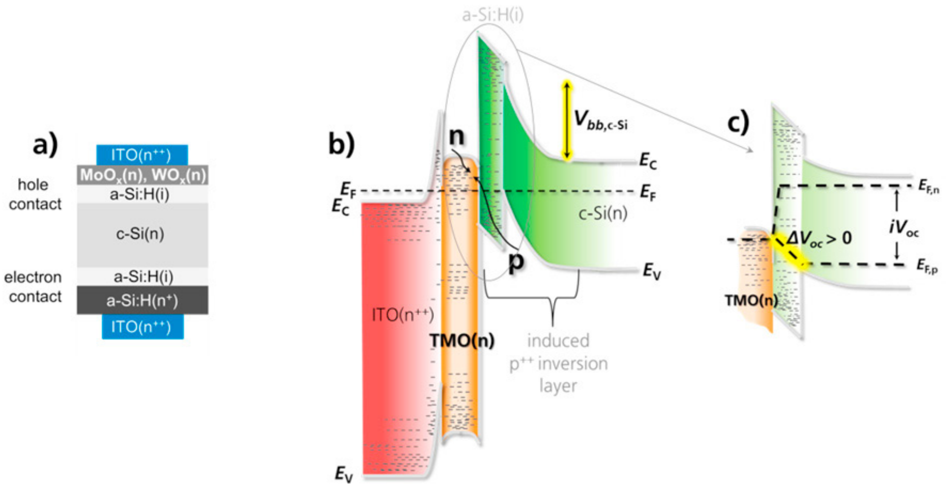

Fig. 1: a) Solar cell precursor used for investigations. b) Possible equilibrium band diagram of investigated hole contact, the induced c-Si band bending is highlight in yellow c) Band diagram during operation, non-ideal hole selectivity is indicated by the significant gradient in the hole majority carrier Fermi-level (yellow).

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 MoO_x and WO_x films and the sputter damage reactive sputtering in the DC mode from a molybdenum or tungsten target with a variable O_2 content (OC) in the sputtering gas [OC = $O_2/(O_2+Ar)$] 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. iNin precursors featured good surface passivation before deposition of the TMO, quantified by an implied V_{oc} 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 (V_{bb} in Fig. 1b), the external V_{oc} and the implied V_{oc} (iV_{oc}) of simple small area solar cell precursors. It allows identifying weather the passivation (iV_{oc}) or an insufficient selectivity are dominating the electrical losses of the investigated contact. By comparing the V_{oc} and iV_{oc} we probe whether the contact fulfills one basic requirement of the ideal diode theory [13], [14], which is a negligible gradient in the Fermi-level of the contacts majority carriers. Accordingly, $\Delta V_{oc} = iV_{oc} - V_{oc} > 0$ eV (Fig. 1c) will indicate that 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 ΔV_{oc} 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. V_{bb} 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, V_{bb} provides indirect information on the effective work function [17] which is determined by the MoO_x bulk and the interfacial MoO_x 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 MoO_x 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 iV_{oc} up to 705 mV can be reached for OC > 0 %. Fig. 2b shows that external V_{oc} of the sputtered films is limited to below 620 mV which means that $\Delta V_{oc} = iV_{oc} - V_{oc} \gg 0$ (Fig. 2c). Accordingly, the performance of all sputtered contacts is limited by an insufficient ability of the MoO_x 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 (ΔV_{oc}) is only improved for the 150°C annealing (red) and decreased for higher temperatures. This interplay leads to the fact that the highest external V_{oc} 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 V_{bb} defines the asymmetry of the hole / electron density of the induced (p/n) junction during equilibrium. Hence, a certain value of V_{bb} (basically $V_{bb} > V_{external}$) is needed to maintain this asymmetry (i.e. low-

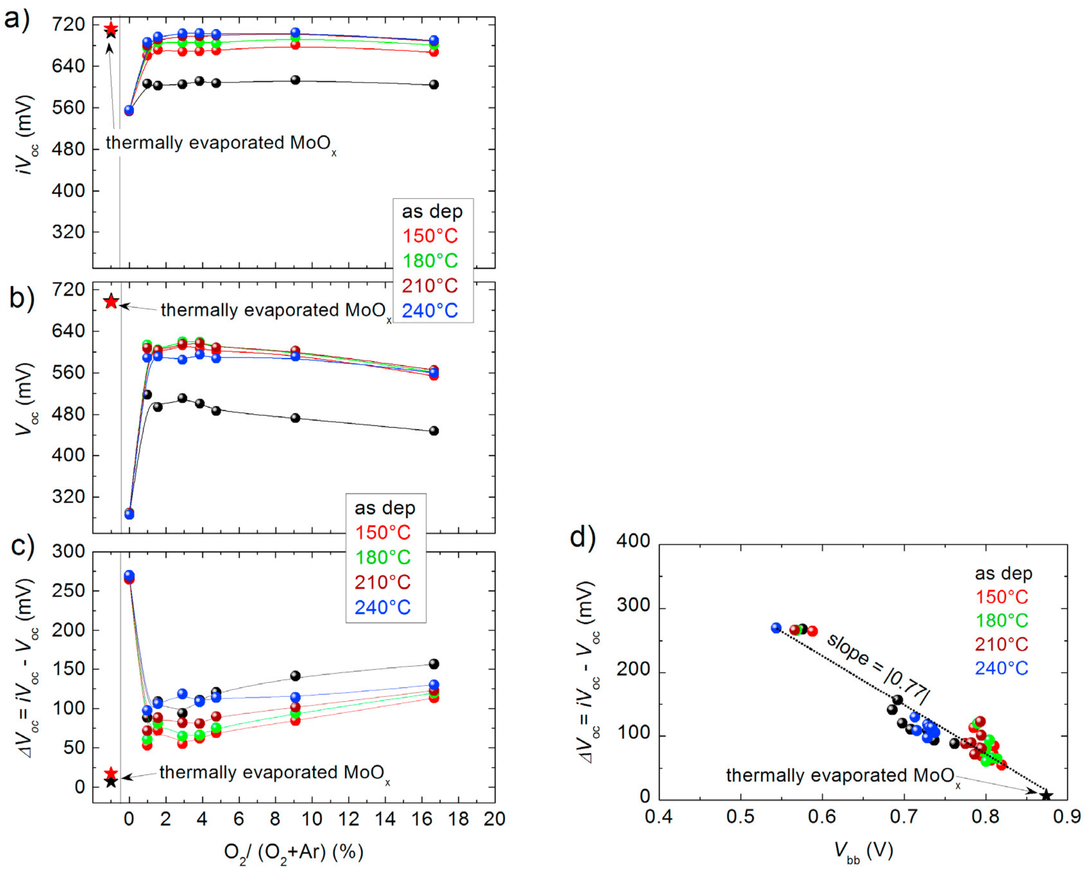

Fig. 2: Results from the variation of the oxygen content in the sputtering gas during sputtering from a Mo target for different post-deposition annealing temperatures.

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 ΔV_{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 ΔV_{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 ΔV_{oc} is even worse compared to the sputtered MoO_x contacts. The optimum OC seems slightly higher and is near 3 %. The dependence of ΔV_{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.

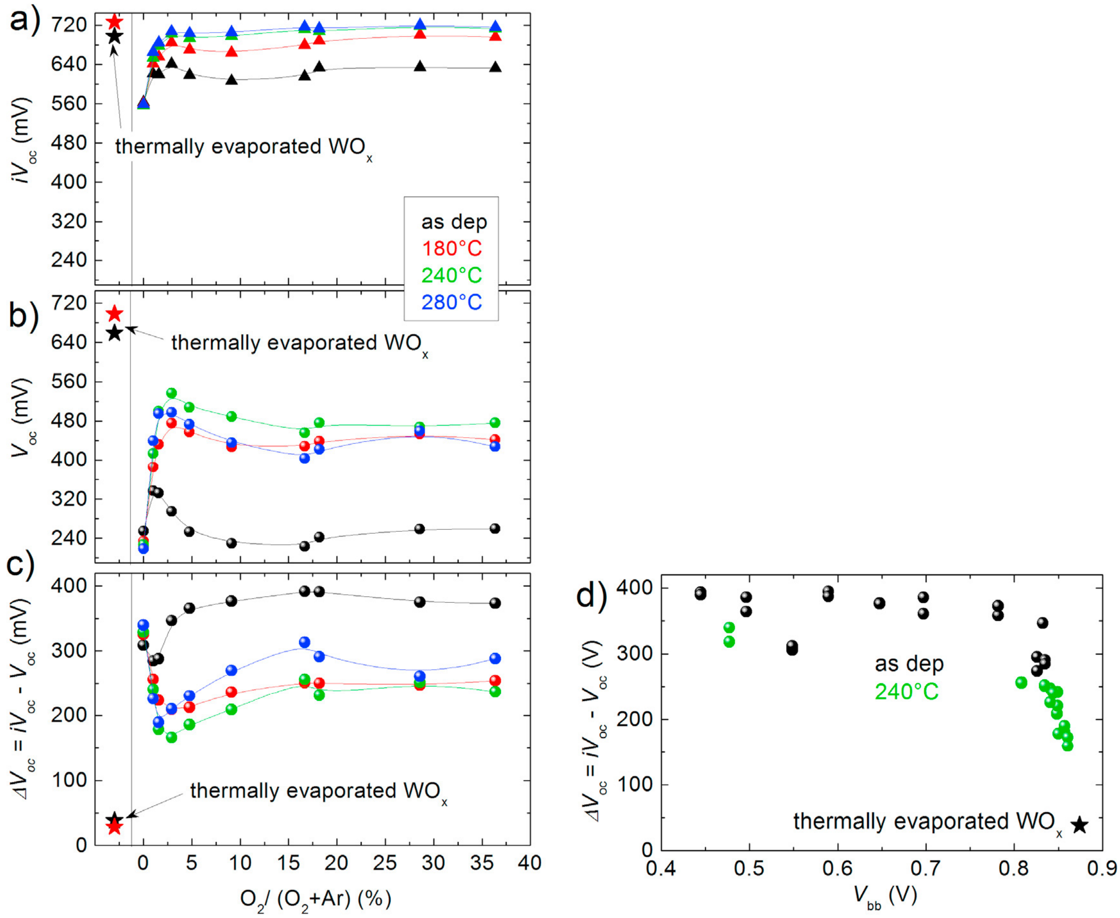

Fig. 3: Results from the variation of the oxygen content in the sputtering gas during sputtering from a W target for different post-deposition annealing temperatures. It should be noted that, unlike Fig. 2d, V_{bb} in Fig. 3d was not measured on the same samples as those used to determine ΔV_{oc}. A 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.

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.

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