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Molybdenum and tungsten oxide: High work function wide band gap contact materials for hole selective contacts of silicon solar cells

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ABSTRACT

The high work function metal oxides, tungsten oxide (WO_x) and molybdenum oxide (MoO_x), were investigated regarding their ability to form a hole-selective contact for a crystalline silicon absorber. We show that in principle both materials have the potential to (i) either replace the p-type amorphous silicon thin films typically used as the high work function contact material in silicon based heterojunction solar cells or (ii) to assist the hole extraction if used as an additional contact layer placed between the p-type amorphous silicon and the TCO electrode. For an integral evaluation of the actual loss mechanisms limiting the contact characteristics both the ability of the contact scheme to passivate the absorber and to selectively extract the excess holes from the absorber are analyzed.

1. Introduction

The selective extraction of the absorber's excess holes and electrons into the external circuit is largely defined by the conductivity of the device regions in close proximity to the external metal electrodes. These device regions form the hole and electron selective contacts of a solar cell [1,2]. More precisely, in these device regions the conductivity of the carrier species that shall be blocked must be as small as possible. As for the other species, for which the contact is intended to be selective, the local conductivity must be sufficiently high to guarantee a lossless carrier transport into the external electrodes. Experimentally, such an extreme asymmetry of the local conductivity is mainly achieved by a strong asymmetry of the local hole (p) and electron (n) densities, which result from sufficient doping and/or an induced junction. Both doping and the induced junction must be designed in such a way that they result in the desired formation of local p^+ or n^+ regions for which $p >> n$ and $n >> p$ are maintained for all working conditions, respectively. This prerequisite is synonymous to the requirement to maintain low-injection conditions in the contact region, i.e. the contact's majority carrier density must remain well above the contact's minority carrier density during operation. The way in which low-injection conditions are ensured is the decisive difference between the classical homojunction and the rather novel or rediscovered approaches, often referred to as passivated contacts [3]. For the classical homojunctions, the experimental approaches used to obtain a preferred hole/electron transport always come at the cost of an increased minority carrier recombination. Depending on the actual junction design, major losses arise from the fact that (i) the metallized regions contacting the doped c-Si regions are not passivated and hence exhibit a high recombination activity and (ii) the heavy doping effects of the doped p^+ and n^+ c-Si regions (increased Auger recombination and band gap narrowing). The class of passivating and carrier-selective contact schemes allows one to avoid these intrinsic losses to a large extent. Their basic features rely on the contact schemes applied to conductor–insulator–semiconductor solar cells [4]. Basically, for the passivation of the absorber, high band gap buffer layers like silicon oxide (SiO_x) and amorphous silicon (a-Si:H (i) featuring a low defect density are placed on the absorber's surface. The low defect density enables the chemical passivation of the absorber and the high band gap greatly decouples the defects in the contact layer and the metal or metal-like TCO electrodes from its influence on c-Si passivation. To obtain carrier selectivity, contact layers featuring a suitable work function and a sufficiently high carrier density (metals, doped silicon thin films, metal oxides) are placed on top of the buffer layer to induce a p^+ or n^+ region in the c-Si absorber (and the buffer). In particular, the silicon based heterojunctions (SHJ) [5] for which undoped a-Si:H buffer layers and doped a-Si:H contact layers are applied have proven that carrier selectivity can be obtained virtually without adding recombination losses. This is quantified by a very high V_{oc} of up to

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750 mV [6], which is only about 10 mV below the upper limit defined by the intrinsic recombination of the high quality crystalline silicon absorber [7]. Such devices show not only nearly ideal performance at open-circuit conditions but the very high efficiencies and high *FFs* reveal that the performance at MPP conditions can be excellent as well. However, some intrinsic challenges come along with the application of a-Si:H. (i) The doping efficiency of a-Si:H is rather low. This applies in particular to the p-doped films [8]. Their low net doping and high defect density make the optimization of the hole contact typically more challenging than that of the electron contact. As a minimum thickness (and doping) of the a-Si:H has to be a applied to form the junction [9,10] (ii), the parasitic photon absorption in the doped a-Si:H lowers the carrier generation in the absorber significantly [11]. (iii) The temperature stability of a-Si:H is limited to below 200 °C [12], which calls for adapted process steps for back end processing (TCO, metallization) and module integration, both of which are hardly compatible with the well-established mainstream processes used for homojunction cells. The latter facts are the main driver for research in alternative passivated contact schemes.

In this paper we concentrate on evaluating alternative contact layers based on high work function metal oxides, a class of materials which is widely used for organic electronic devices to form hole-selective contacts [13,14]. More precisely, the applicability of molybdenum oxide (MoO_x) and tungsten oxide (WO_x) to either (i) replace the p-type a-Si:H of the standard SHJ or (ii) to act as an additional contact layer to improve the work function matching at the parasitic Schottky contact formed between the TCO electrode and the a-Si:H(p) is investigated (Fig. 1).

A motivation for the experimentally investigated approaches on the basis of device simulations is given in Refs. [10,15]. Besides the general characteristics of the solar cells, the non-ideal junction behavior which follows from a poor hole extraction, mainly caused if the contact region is operating in high-injection conditions, are also discussed there. Potential benefits from using such high work function films for the hole selective contact are indicated in the following. In the case of (ii), where a high work function film is added as an additional contact layer to the standard SHJ structure (Fig. 1c), the required a-Si:H(p) thickness and doping should be lower. This follows from the fact that the parasitic Schottky junction induced into the a-Si:H(p) should be less pronounced. Experimentally, the importance of such an additional contact layer to improve the TCO/doped a-Si:H contact was recently investigated in Ref. [16] for WO_x. For case (i), where the doped a-Si:H is omitted and replaced by such a high work function film (Fig. 1b), the improvement of the optical properties is one major concern. The basic applicability of MoO_x and the reduced parasitic absorption caused by the higher optical band gap of MoO_x have been shown by Battaglia et al. [17] recently. Unfortunately the improvement of the J_{sc} was accompanied by a degradation of the electrical properties (mainly *FF*). However, besides better optical properties, metal oxides might also lower the recombination losses or relax the requirements on the buffer layer with respect to surface passivation. This is deduced from investigations where a buffer layer is omitted. Without a buffer layer, reasonable surface passivation for the investigated WO_x/c-Si contact was observed which was superior to that of the a-Si:H(p)/c-Si contact where the highly defective a-Si:H(p) is in direct contact to the absorber. Unlike for our investigations, reasonable surface passivation was also recently observed for the MoO_x/c-Si contact by Bullock et al. [18].

The second focus of this work is on the characterization approach which we typically apply to identify if the cell parameters (*FF* and V_{oc}) of such alternative contact schemes are limited by a non-ideal carrier extraction [19,15]. It will be shown that analyzing distinctive features of the illumination level dependence of the V_{oc} provides an easy means to evaluate if the external contact characteristic obeys the standard p/n-junction theory for which minority carrier recombination (c-Si passivation) and ohmic transport losses are of major concern, or, if the ability of the contact scheme to selectively extract the absorber's excess carriers is a limiting factor.

It should be noted that the discussion here is mainly based on the induced junction and its ability to provide a sufficiently high hole density to maintain low-injection conditions in the contact region. However, it is likely that other effects like the increase of the tunneling current with increasing hole density and the properties of the metal oxide/a-Si:H(i) and the ITO/metal oxide heterojunctions will affect the selective hole extraction as well. A sensitivity analysis by means of device simulations is on the way to shed more light on the influence of such factors.

2. Experimental

2.1. Solar cells

To evaluate the electrical and optical properties of the different contact schemes by *J–V* and quantum efficiency measurements, simple planar small area (2×2 cm^2) solar cells were fabricated on 4 in. shiny-etched float-zone 1 Ω cm *n*-type silicon wafers. After wet chemical cleaning of the c-Si absorber, nominally undoped and p- or n-doped a-Si:H films were deposited by PECVD. For all configurations the electron selective contact (forming the BSF) consists of a c-Si(n)/a-Si:H(i)/a-Si:H(n) stack at the rear which is finished by a thermally evaporated stack of Ti/Pd/Ag. The variations of the hole selective contact (emitter) at the front are shown

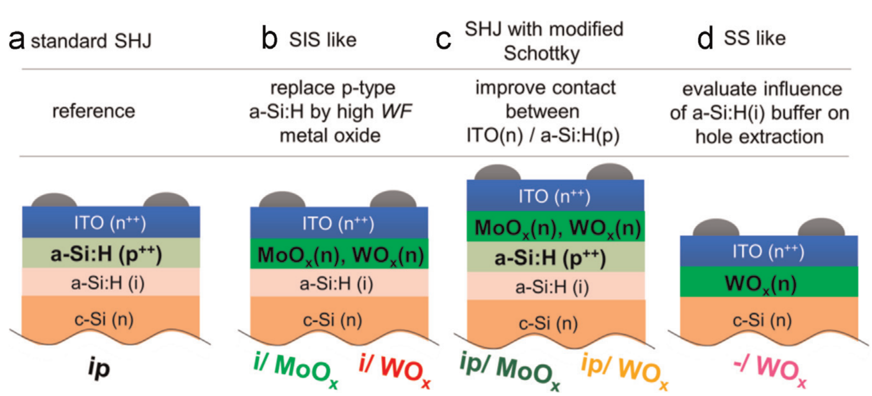

Fig. 1. Schematic of investigated front sides which form the hole selective contact of simple planar solar cells. Above the sketches is the motivation for the respective structure. Below the sketches the acronyms used throughout this work to distinguish between the different structures are shown.