

Transport mechanisms in silicon heterojunction solar cells with molybdenum oxide as a hole transport layer



R. García-Hernansanz^{a,*}, E. García-Hemme^a, D. Montero^a, J. Olea^a, A. del Prado^a, I. Mártel^a, C. Voz^b, L.G. Gerling^b, J. Puigdollers^b, R. Alcubilla^b

^a Dept. de Física Aplicada III (Electricidad y Electrónica), Univ. Complutense de Madrid, 28040 Madrid, Spain

^b Departament d'Enginyeria Electrònica. Universitat Politècnica de Catalunya, 08034 Barcelona, Spain

ARTICLE INFO

Keywords:

Molybdenum oxide
Multitunneling
Gap states
Heterocontact

ABSTRACT

Heterojunction solar cells based on molybdenum sub-oxide (Mo_xO_x) deposited on n-type crystalline silicon have been fabricated. The hole selective character of Mo_xO_x is explained by its high workfunction, which causes a strong band bending in the Si substrate. This bending pushes the surface into inversion. In addition, the sub-stoichiometry of the evaporated Mo_xO_x layers leads to a high density of states within the bandgap. This is crucial for charge transport. The J-V electrical characteristics at several temperatures were analysed to elucidate the dominant charge transport mechanisms of this heterojunction structure. We have identified two different transport mechanisms. At low bias voltage, transport is dominated by hole tunnelling through the Mo_xO_x gap states. At higher voltage the behaviour is similar to a Schottky junction with a high barrier value, due to the high Mo_xO_x work function. These results provide a better understanding of the hole selective character of Mo_xO_x /n-type silicon heterocontacts, which is key to further improve this new kind of solar cells.

1. Introduction

The present record energy conversion efficiency of silicon-based solar cells is 26.3% [1], which is close to the Shockley–Queisser limit for a single junction silicon solar cell [2]. Such a high efficiency has been achieved by Kaneka combining the HIT (Heterojunction with Intrinsic thin Layer) concept with an interdigitated back contact (IBC) structure. This record efficiency exceeds by 1% the best silicon homojunction solar cells [3]. Nevertheless, conventional silicon p-n junctions still dominate the solar cell market owing to their simpler fabrication, which enable lower manufacturing costs. The need of comparatively complex PECVD deposition systems and the need of hazardous precursors slow down the adoption of heterojunction technology.

A limitation of conventional two-side HIT solar cells is the parasitic light absorption of amorphous silicon layers, which reduces the photocurrent [4]. On the other hand, the absence of high temperature processes makes this technology more processing-friendly with thinner wafers, as opposed to conventional homojunction solar cells. These standard cells also have other limitations such as recombination losses [5] and heavy doping effects [6], which impose a limit on their efficiency.

In the last few years several works have been published aiming to replace doped emitters of classical Si junctions with alternative

materials. The aim is to achieve a “carrier-selective” interface with the absorber [7–9]. The charge separation occurs because one type of charge is blocked while the flow of the opposite one is allowed [10]. The incorporation of such carrier selective heterocontact structures could improve some fundamental limitations of conventional solar cells. Furthermore, most of these materials can be deposited by evaporation or even solution-processed [11]. If these simple technologies could be integrated in a commercial route then higher-efficiency cells could be cost-effectively manufactured. There are different materials reported in the literature that have demonstrated excellent carrier-selective properties on c-Si: organic films [12,13], fluoride salts [8,14] or transition metal oxides (TMOs) [15,16]. At present, organic semiconductors are unstable when exposed to the atmosphere and suffer photodegradation effects [17]. For this reason, inorganic alternatives in combination with silicon absorbers are actively researched. Lithium fluoride [8,18], and titanium dioxide [19] layers have been used as electron collectors on n-type Si substrates, while molybdenum oxide (MoO_x) and tungsten oxide (WO_x) have been used as hole collectors also for n-type Si [20–22]. Recently, a conversion efficiency of 22.5% has been obtained for a solar cell with a MoO_x hole collector on n-type silicon [23]. However, this device still required a very thin intrinsic amorphous silicon layer between the silicon substrate and the MoO_x layer for interface passivation.

* Corresponding author.

E-mail address: rodgar01@ucm.es (R. García-Hernansanz).

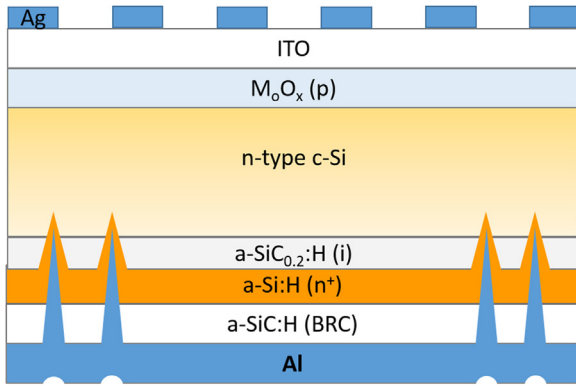


Fig. 1. MoO_x solar cell structure fabricated for this study. The MoO_x layer acts as a hole selective contact on n-type silicon.

TMOs have been studied in depth for organic semiconductor devices [24–26], for electronic applications [27,28] and more recently some works have studied these materials deposited on silicon heterojunctions. The physical principles explaining the collection of photo-generated charge-carriers in these devices have been proposed by Battaglia et al. [22]. Nevertheless, a deeper understanding of the mechanisms governing charge-carrier transport without illumination is still needed. An accurate analysis and understanding of the J-V electrical characteristics in dark can provide guidelines to improve the V_{oc} values of these devices.

2. Experimental methods

In Fig. 1 we present the structure of the MoO_x heterojunction solar cells studied in this work. The substrate was a double-side polished, 300 μm thick, n-type (2.5 Ω cm) crystalline silicon wafer. First, the substrate was cleaned by a standard RCA cleaning process with a subsequent dip in HF solution (1%) until it became hydrophobic. Then, it was loaded into a PECVD system to deposit a stack of layers on the rear side. This stack consisted of a 4 nm intrinsic a-SiC_x:H (x~0.2) passivation layer and a 15 nm phosphorous-doped a-Si:H layer. An additional stoichiometric a-SiC_x:H (x~1) layer was deposited to protect the stack and as a back reflector coating (BRC). Afterwards, the rear side was laser-fired to obtain an array of locally-diffused point contacts with a contacted area ratio of 0.5%. This optimized laser process allows to combine low series resistance with reduced surface recombination at the rear contact [29]. On the front side, after another HF dip, a 15 nm MoO_x layer was thermally evaporated directly on the c-Si substrate, without an a-Si:H passivation layer. We cannot discard the presence a thin interfacial SiO₂ layer (~2 nm) between the Si substrate and the MoO_x that grows spontaneously [30]. Subsequently an indium-tin-oxide (ITO) front electrode was deposited by RF magnetron sputtering. Solar cells with 1 cm² and 4 cm² active area were defined by a lithographic process and a wet etching of the ITO and MoO_x layers. The front electrode is finished by thermally evaporating a 2 μm thick silver grid. This electrode covers less than 5% of the device area. Finally, the rear electrode consisted in a 1 μm thick aluminium layer evaporated on the laser-fired contacts.

The current density as a function of applied voltage (J-V characteristic) was measured with an Agilent 2400 SourceMeter. The J-V curves were measured in darkness and under 1-sun AM1.5 illumination with an ORIEL 94021A (Newport) solar simulator. The light irradiance was properly calibrated by means of a pyrometer. The external quantum efficiency curve was measured using a commercial instrument QEX10 from PV Measurements. After the initial room temperature characterization, the solar cell was mounted inside the chamber of a closed-loop helium cryostat, which controls temperature with an additional heater. Then, J-V characteristics in darkness were measured at

temperatures from 360 K to 220 K. All these electrical measurements were done in a 4 wire configuration to minimize the contribution of the copper cables to the series resistance. The well-known two-diode model was used to fit the measured J-V curves [31,32] according to the following expression:

$$J = J_{D1} + J_{D2} + J_{SHUNT}$$

$$J = J_{0,1}(T)[e^{A_1(T)(V-JR_S)} - 1] + J_{0,2}(T)[e^{A_2(T)(V-JR_S)} - 1] + \frac{V - JR_S}{R_{Shunt}} \quad (1)$$

In this expression J_{D1} and J_{D2} correspond to the two main conduction mechanisms, where $J_{0,1}(T)$ and $J_{0,2}(T)$ are the saturation current densities and $A_1(T)$, $A_2(T)$ are the exponential factors of each mechanism. Also, the parasitic series resistance R_S and parallel resistance R_{Shunt} were considered in the equivalent circuit. We can determine the different conduction mechanisms by studying the temperature dependences of the fitting parameters of Eq. (1). It is known that the saturation current density and the exponential factor will adjust to the following expressions [33,34]:

$$J_{0,i} = J_{0,0,i} e^{-\frac{E_{a,i}}{kT}} \quad (2)$$

$$A_i(T) = \frac{q}{n_i kT} \quad (3)$$

where $E_{a,i}$ is the activation energy of each mechanism and n_i the corresponding diode ideality factor. Finally, to analyse the electrical characteristics measured at reverse bias polarization we used the following equation [31,35]:

$$J_R = J_{rev,0} e^{\left(-\frac{E_{a,rev}}{kT}\right)} (V_D - V)^b \quad (4)$$

where $J_{rev,0}$ is a base current, V_D a constant voltage, $E_{a,rev}$ an activation energy of the process and b is a temperature independent coefficient.

3. Results and discussion

Fig. 2 shows the EQE and J-V characteristic curve of a representative MoO_x based solar cell at room temperature under 1-sun illumination. All the fabricated devices showed a similar behaviour, either for 1 cm² or 4 cm² cells. These solar cells have a V_{oc} = 614 mV, J_{sc} = 32.8 mA/cm² and F.F. = 73.2%, resulting in a photovoltaic conversion efficiency of 14.7%. To our knowledge this is the best efficiency reported for a direct heterojunction between MoO_x and n-type c-Si without passivation layers. The V_{oc} and F.F. values are significantly higher than those previously reported [9]. The J_{sc} value is lower in our cells, but is rather good for a non-textured surface.

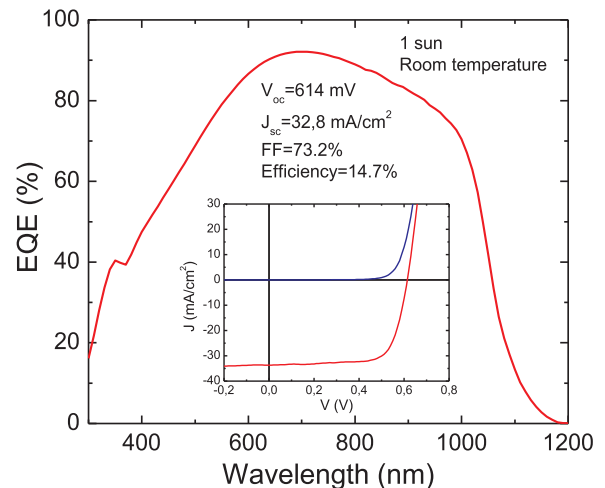


Fig. 2. J-V and EQE characteristic of a MoO_x based solar cell under illumination at 1 sun at room temperature.

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