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Heterojunction solar cells with asymmetrically carrier-selective contact structure of molybdenum-oxide/silicon/magnesium-oxide

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ABSTRACT

New functional materials that are constantly introduced into carrier-selective contacts (CSCs), which allow one type of carrier passing through while blocking the other type *via* energy band alignment at contact region, promote the fabrication of crystalline silicon (c-Si) solar cells towards low-temperature and dopant-free. Here, electron-beam-evaporated molybdenum oxide (MoO_x) and magnesium oxide (MgO_x) are directly deposited upon the front and rear surface of c-Si substrates, respectively, to form CSCs with asymmetric band offset for holes and electrons. Contact resistivity, passivation effect, interfacial structures and chemical states for both MoO_x/c-Si and MgO_x/c-Si are systematically characterized. Considering good carrier-selectivity at the front and the rear side, the optimum thickness in terms of contact resistivity and photovoltaic performance is 10 nm for MoO_x and 1.5 nm for MgO_x, respectively. Finally, an efficiency over 14% for the planar MoO_x/c-Si/MgO_x heterojunction solar cells is achieved, demonstrating huge economic potential in fabrication procedure over conventional high-temperature diffused homojunction solar cells.

1. Introduction

Carrier-selective contacts (CSCs) with favorable energy band alignment now have been paid much interest for crystalline silicon (c-Si) solar cells due to the extraordinary capability in separation and collection on photo-generated carriers. Relying on the nearly ideal asymmetric band offset designs at CSC regions, only one type of photo-excited carrier (electrons or holes) can be allowed to transport, so the interfacial recombination will be greatly suppressed and the devices may have extremely high open-circuit voltage (V_{oc}) and efficiency. Based on low-temperature or even solution-proceeded procedures, functional materials including transition metal oxides (Battaglia et al., 2014a,b; Sun et al., 2017; Um et al., 2016; Wang et al., 2017), carbon nanotube (Wang et al., 2015; Xu et al., 2016b), graphene (Diao et al., 2017;Xu et al., 2016a), organic polymers (Chen et al., 2017; He et al., 2017, 2016; Liu et al., 2014; Mu et al., 2015), alkali metal fluorides (Wan et al., 2016), and titanium oxide (Allen et al., 2017; Liu et al., 2017) *etc*, have been explored and demonstrated as good CSC layers to *n*-type c-Si (n-Si) absorbers. By now, with the additional help of high quality interfacial passivation provided by the intrinsic amorphous silicon thin layers, promising efficiencies of 19.4% and 22.5% have been reported for the Si solar cells featuring double-sided and front-sided dopant-free CSCs, respectively(Wan et al., 2016; Geissbühler et al., 2015).

From a band alignment view, when contacting high work function metal oxides (MoO_x, VO_x, WO_x, NiO_x, CuO_x) (Almora et al., 2017; Bullock et al., 2014; Gerling et al., 2016; Kim et al., 2016; Meyer et al., 2012; Park et al., 2016; Wu et al., 2017) with *n*-Si, a large conduction band offset will be formed at the Si surface, leading to a strong inversion layer with accumulation of holes. The heterojunction works more like a p^+n junction and enables a high enough theoretical built-in potential. Meanwhile, the Schottky barrier is usually formed by directly contacting the metal electrode with a moderate doped *n*-Si substrate (for example Si/Al contact), hindering the electrons transport at the rear side. Low work function metal oxides (TiO_x, MgO_x) (Liu et al., 2017; Wan et al., 2017; Yang et al., 2016), which have small conduction band offset with *n*-Si, are promising candidates to be inserted between Si/Al interface to alleviate the Fermi level pinning effect and reduce the energy barrier for electrons. In this kind of CSCs, the contact quality is determined by several key parameters including contact resistivity, recombination rate, built-in voltage, *etc*, which are all vital factors for achieving high efficiency. Therefore, for the CSCs with typical

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functional metal oxides, systematic investigations need to be synchronously emphasized on contact resistivity, interfacial structures and passivation.

In this work, we demonstrated solar cells with asymmetric CSC structures, of which electron-beam evaporated MoO_x and MgO_x were employed as hole and electron transporting layer on the front and rear side of c-Si substrate, respectively. The current density-voltage curves, minority carrier lifetime and interfacial structures for both MoO_x/Si and MgO_x/Si contacts were investigated. The optimum thickness in terms of contact resistivity is 10 nm for MoO_x and 1.5 nm for MgO_x, respectively. External quantum efficiency spectra (*EQE*), capacitance–-voltage (*C–V*), Scanning Kelvin probe microscopy (SKPM) and X-ray photoelectron spectroscopy (XPS) measurements confirmed the positive roles of MgO_x in reducing the barrier height and suppressing the carrier recombination at Si/Al interface. Finally, planar heterojunction solar cells with a core structure of MoO_x/c-Si/MgO_x were fabricated with efficiencies up to 14.2% *via* a dopant-free and low-temperature fabrication procedure, demonstrating new possibilities in designing and fabricating low-cost optoelectronic devices.

2. Experimental section

One side polished *n*-Si wafers (CZ, 100 Orientation, 1–3 Ω·cm) were used to fabricate the solar cells with the configuration of Ag-grid/ITO/MoO_x/*n*-Si/MgO_x/Al. The Si substrates were firstly cleaned by a standard RCA cleaning process prior to a dipping in diluted hydrofluoric acid (5%, 2 min, to remove the native oxide), and then immediately transferred into the electron-beam evaporator (ZZS500). Under a base pressure of 1×10^{-6} mbar, MoO_x film was deposited from a MoO_3 source crucible with a fixed growth rate of 0.2 Å/s at ambient temperature. Then an 80-nm-thick indium tin oxide (ITO) film was deposited upon the as-fabricated MoO_x layer by an RF magnetron sputter (MRC 603). Silver (Ag) grid with shielding area of 7% was deposited on the front surface as top-electrode by thermal evaporation *via* a hard mask. MgO_x film was deposited onto the unpolished rear surface of *n*-Si by an electron beam evaporator with a fixed growth rate of 0.2 Å/s, by using MgO powder as the source. Finally, the rear electrode was completed by depositing a 300 nm-thick aluminum layer upon the MgO_x layer *via* thermal evaporation.

The thickness of the MoO_x and MgO_x layers was measured by ellipsometry (M-2000DI). The photovoltaic characteristic curves of the solar cells were collected by a Class AAA solar simulator (Oriel, Sol3A) with a Xe-arc lamp under Air-mass 1.5 illumination (1000 W/m^2) in the standard testing condition. The *EQE* curves were measured by a quantum efficiency measurement system (Newport Oriel, IQE-200). The capacitance versus voltage (*C–V*) and the current-voltage (*I-V*) measurements were carried out with a Keithley 4200-scs semiconductor parameter analyzer. The minority carrier lifetime was measured by a microwave photoconductivity decay system (WT-2000 μPCD, Semilab) and a Sinton WCT-120 lifetime tester. Suns-V_{oc} was also measured by the Sinton WCT-120 tester. XPS was conducted using a monochromatic Al Kα X-ray source and a hemispherical analyzer in ultrahigh vacuum with a base pressure of 1×10^{-10} mbar (Kratos AXIS Ultra DLD). The morphology of the MgO_x interlayer was identified by a high resolution transmission electron microscopy (TEM, Tecnai F20). Transmittance was measured using a Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer equipped with a 150-mm-diameter integrating sphere by excluding those of the substrate. Surface potential image was obtained using Scanning Kelvin probe microscopy (SKPM) measurement (VEECO, Dimension 3100 V).

3. Results and discussion

3.1. Photovoltaic structure of CSCs

Fig. 1(a) presents the structure of the dopant-free solar cells equipped with Ag-grid/ITO/MoO_x/*n*-Si/MgO_x/Al stack. The schematic of energy band diagram is shown in Fig. 1(b). The MoO_x with a measured work function of 5.4 eV can be regarded as a hole-selective or transporting layer, which can induce a strong inversion layer near the *n*-Si surface due to the huge conduction band offset (Gerling et al., 2017). The high density of defect states inherent to the oxygen deficiencies is believed to beneficial to holes transport (Battaglia et al., 2014a,b). Besides, the MoO_x with high transparency and low absorption in visible wavelength range can serve a good window layer in terms of the optical properties as shown in Fig. S1. Meanwhile, MgO_x with a measured work function of 2.8 eV is selected as an electron-selective layer to achieve low contact resistivity, facilitating the transport of electrons (Brennan et al., 2015).

3.2. Photovoltaic performance of CSCs

The current density-voltage (*J-V*) characteristics of the solar cells with and without MgO_x interlayer are plotted in Fig. 2(a). The photovoltaic performance parameters of V_{oc}, short circuit current density (J_{sc}), fill factor (*FF*) and power conversion efficiency (*PCE*) for the solar cells featuring different thickness of MgO_x interlayer are summarized in Table 1. The insertion of 1.5 nm MgO_x layer improves all photovoltaic performance parameters with V_{oc} from 0.578 V to 0.595 V, J_{sc} from 31.2 to 32.6 mA/cm^2, and *FF* from 68.8% to 73.4%. This yields a *PCE* of 14.2%, 15% enhancement from 12.4% of the reference solar cells. With an absolute enhancement of 4.6%, *FF* receives the largest gain among all the photovoltaic performance parameters parameters. When the thickness of MgO_x is below or above 1.5 nm, the photovoltaic performance degrades consistently with the contact resistivity results from Fig. 3(b). The insertion of MgO_x can also improve the passivation quality, as shown by the Suns-V_{oc} measurements in Fig. 2(b), indicating by the enhanced V_{oc} under higher light intensity. Higher light intensity leads to more minority carriers injected into the device, indicating that fewer minority carriers are sacrificed at the rear surface for the rear contact with MgO_x thin layer. In presence of 1.5 nm MgO_x, the V_{oc} was promoted from 578 mV (reference cell) to 595 mV. External quantum efficiency (*EQE*) spectra were measured to investigate the carrier collection efficiency ranging from 300 to 1200 nm, as shown in Fig. 2(c). The insertion of MgO_x enhances the *EQE* response ranging from 300 to 1200 nm, especially for the longer wavelengths (mainly 900–1100 nm range), which is due to that the *n*-Si/MgO_x/Al rear-side contact design could reduce the barrier height and suppress the carrier recombination. As shown in Fig. 2(d), the built-in voltages (V_{bi}) calculated from the *C-V* measurements also confirm the positive effect of MgO_x interlayer on the suppression of potential loss at the rear side. Due to the presence of surface (gap) states a considerable fraction of the potential difference to drop over a very thin dipole layer at the semiconductor/metal interface. The ultrathin MgO_x layer is inserted to passivate interface defects while allowing majority carrier transport to a doped semiconductor(Würfel et al., 2014). The results indicate that the insertion of MgO_x layers can dramatically improve the photovoltaic device performance in accordance to recently published results (Wan et al., 2017).

3.3. Contact resistivity and passivation effect of the two metal oxides

The contact resistivity (ρ_c) of the MoO_x/*n*-Si and MgO_x/*n*-Si structures is measured, as shown in Fig. 3(a) and 3(b), respectively. For the MoO_x/*n*-Si contact, a transfer-length-method (TLM) contact pad array is employed to calculate ρ_c. As shown in the inset of Fig. 3(a), 20/250 nm-thick Pd/Ag metal patterns are deposited upon the MoO_x film and served as the electrodes. From the Fig. 3(a), one can find that the ρ_c of MoO_x/*n*-Si decreases abruptly from above 800 mΩ·cm^2 to around 30 mΩ·cm^2, with the thickness of MoO_x film increasing from 5 nm to 10 nm. This trend may be caused by the configuration changes of the deposited MoO_x from discrete islands to a continuous thin film. However, when the thickness of MoO_x film increasing from 10 nm to 30 nm,