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Band alignment of CdTe with MoO_x oxide and fabrication of high efficiency CdTe solar cells

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ABSTRACT

The band alignment of CdTe/MoO_x hetero-interface contact at back electronic electrode in CdTe thin film solar cell was quantitatively characterized by photon electron emission spectroscopy. The experimental results showed that depending on the CdTe surface chemical state and the stoichiometric value of x in MoO_x, energy barrier with a value as low as 0.23–0.39 eV was developed at the CdTe/MoO_x contact interface for a MoO_x buffer layer with an x value of 2.86–3. CdTe solar cell with relatively high efficiency can be fabricated by using a MoO_x as a back contact buffer, which is allowed to have a relatively large stoichiometric x range of 2.86–3. The Te-rich CdTe surface obtained by chemical etching induced a reduction reaction upon the deposition of a MoO_x thin layer, leading to the formation of reduced Mo states and other defect states below the Fermi level, which assisted hole carrier transport.

1. Introduction

CdTe thin film solar cell has been drawn intensive attention in the photovoltaic research community in the last two decades. The efficiency of small-sized CdTe solar cell has been increased dramatically from 16.5% to 22.1% in the last several years (Green et al., 2012, 2016). CdTe is a II–VI semiconductor with a direct band gap energy of 1.45 eV, and its light absorption coefficient is of the order of $10^5\,cm^{-1}$ for the photons with energy higher than the band gap. Therefore CdTe can efficiently absorb the sun light radiation and CdTe thin film with thickness in several micrometers is enough for the fabrication of a solar cell. Compared to Si-based crystalline solar cell, even though CdTe solar cell efficiency has been increased dramatically in the recent years, the cell efficiency is still much lower than the theoretically predicted value of 29% (Morales-Acevedo, 2006). Several basic problems regarding both the materials and the cell device design/fabrication have long been remained to be unresolved. These problems include efficient p-type doping for CdTe, the control of the formation of native point defects, understanding the defect chemistry, carrier transport in cell structure, the formation of a relatively large energy barrier for hole transport at the CdTe/metal contact, and the relatively low open-circuit voltage of CdTe thin film solar cell.

Among the problems mentioned above, a stable and low energy barrier at the CdTe cell back contact is much desired for both CdTe solar cell fabrication and long-term employment of CdTe solar cell module electric power generation (McCandless and Dobson, 2004). With a work function value of 5.70 eV, it is difficult to form a low resistive ohmic contact at the back contact of a CdTe solar cell. The high contact resistance between CdTe and a back contact is one of the major sources contributing to the device series resistance and a limiting factor for the open-circuit voltage. To obtain a low resistance contact on CdTe, several techniques have been developed or proposed. One is doping the CdTe surface to an electronically degenerate level, and this is usually done by deposition of a thin Cu layer with a thickness of several nanometers (Enzenroth et al., 2009; Wu et al., 2007). Highly doped surface region in CdTe assists the carrier tunneling through the back barrier at the CdTe/metal interface (Bonnet and Mayers, 1998). One of the other methods is to insert a buffer layer between CdTe and the metal electrode. The buffer layer must have a high work function, so that the CdTe/buffer/metal heterojunction forms a band alignment, whose electronic structure can efficiently assist hole transport/injection from the CdTe layer to a metal electrode (Kumar and Rao, 2014). In our laboratory we have employed V_2O_5 as a buffer layer between CdTe and metal electrode in the back contact of CdTe solar cells. A much lower electronic barrier contact was formed compared to the cells with an Au-only metal contact (Shen et al., 2016c). Also CdTe thin film solar cells

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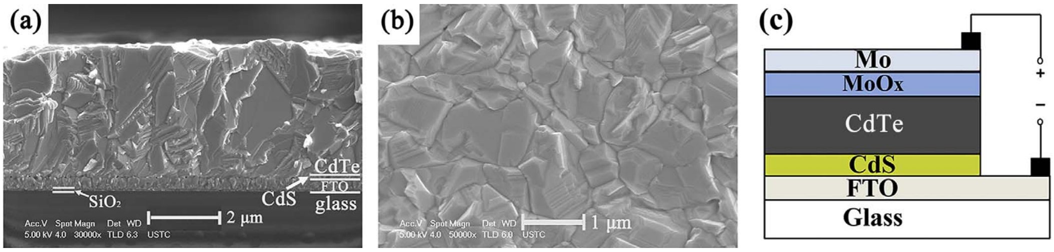

Fig. 1. (a) and (b) SEM cross-sectional and surface morphology of a 4-µm-thick CdTe film on Glass/SiO_2/FTO/CdS; (c) Schematic CdTe solar cell structure with MoO_x oxide as a buffer layer at the back contact.

using an oxide buffer layer at the back contact had been tested to show dramatically enhanced device stability (Shen et al., 2016c; Yang et al., 2016). Molybdenum oxide MoO_x has high work function as high as ~6.80 eV depending on the stoichiometric value of x. In principle ohmic/quasi-ohmic contact can be formed between MoO_x and p-type CdTe. Paudel et al. have studied valence band offset at the MoO_3/CdTe interface by X-ray Photoelectron Spectroscopy (Paudel and Yan, 2014). Solovan et al. have experimentally demonstrated a high quality ohmic electrical contact of MoO_x with p-CdTe single crystal for both DC and AC electrical signals up to the frequency of 10 kHz (Solovan et al., 2016). Irfan et al. have studied the effect of a MoO_x inter-layer at the Ni/CdTe interface. They concluded that a MoO_x layer was effective in reducing the reaction between Ni and the native tellurium oxide at the CdTe surface. The improved solar cell performance was suggested to be based on the evolution of core levels and the valence band at the Ni/MoO_x/CdTe interface, which was ascribed to the MoO_x high work function (Irfan et al., 2012). In this study, we deposited MoO_x oxide layer on CdTe film surface as the contact buffer layer between CdTe and Mo metal electrode. The interface chemical state, the chemical reaction occurred between MoO_x and CdTe, the band alignment at the MoO_x/CdTe interface were systematically studied by employing X-ray photoelectron and photoemission spectroscopy. Highly efficient CdTe thin film solar cells were fabricated with MoO_x oxide as a buffer layer in the back contact.

2. Experimentals

The CdTe thin film solar cells fabricated in this study had a structure of glass/SnO_2:F(FTO)/CdS/CdTe/MoO_x/Mo. The CdS films were deposited on glass substrates coated with F-doped SnO_2 (FTO) (sheet electric resistance of 14 Ω/sq) by the chemical bath deposition technique (CBD). Detailed experimental procedures for CdS film preparation can be found in our previous work (Bai et al., 2011b; Shen et al., 2016b; Yang et al., 2014). P-type CdTe absorber layers were fabricated in a home-made close-spaced sublimation apparatus on glass/FTO/CdS templates. During the film deposition, the CdTe powder source and the substrate temperatures were kept at 640 and 530 °C, respectively. The glass/FTO/CdS/CdTe structures were then subjected to a $CdCl_2$-activation heat treatment in the air atmosphere. The MoO_x oxide films were prepared by reactive magnetron sputtering technique at room temperature. The deposition atmosphere was a mixture of O_2 and Ar with a total pressure of ~1 Pa, the ratio of oxygen was varied from 15% to 30% to obtain stoichiometric suboxides MoO_x and stoichiometric MoO_3. The solar cell Mo metal electrodes, which were prepared in the same chamber and with the same Mo metal target as that of the MoO_x films, were prepared by DC magnetron sputtering. The solar cell size is 0.071 cm^2 (circular area with a diameter of 3 mm). Detailed CdTe solar cell fabrication procedures can be found in our previous works (Bai et al., 2011a; Yang et al., 2014, 2016).

The film morphological and solar cell device microstructures were characterized by using a field emission scanning electron microscope (SEM, Sirion 200). The solar cell current-voltage J-V curves were measured under the standard AM1.5 illumination (1 kW/m^2, 25 °C) using a solar simulator (Oriel Sol 3A, USA). XPS measurements were performed using a Thermo VG Scientific ESCALAB 250 instrument with Al Kα as the X-ray source. All the XPS spectra were calibrated by using the carbon 1s energy level (284.6 eV). Kelvin probe force microscope (KPFM) was employed to characterize film surface potential. Photoemission spectroscopy (PES) measurements were carried out in an ultra-high vacuum chamber at the Photoemission Endstation of the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The Endstation is equipped with a Scienta R3000 hemispherical electron energy analyzer, the resolution of the PES is 0.10 eV.

3. Results and discussions

3.1. Oxide MoO_x thin film and CdTe solar cell fabrication

The cross-sectional microstructure of a CdTe solar cell fabricated in this study is shown in Fig. 1a. The CdTe solar cell had a structure of glass/SnO_2:F(FTO)/n-CdS/p-CdTe/MoO_x/Mo, as schematically shown in Fig. 1c. Fig. 1b shows the surface morphology of a CdTe film grown on a glass/SnO_2:F(FTO)/n-CdS substrate. The CdTe film was polycrystalline and most of the CdTe grains showed through-film-thickness microstructure as can be seen in Fig. 1a. Such a p-type absorption layer is beneficial for the transport of photon-generated carrier in CdTe, leading to low carrier recombination and scattering occurred at grain boundaries (Shen et al., 2016a).

Fig. 2a shows the atom force microscope (AFM) image of a $MoO_{2.86}$ film with a thickness of 200 nm. In this study we call this film bulk sample. The film surface was very smooth with an AFM root-mean square roughness of 2 nm. The cross-sectional SEM image of the film, shown in Fig. 2b, indicates a densely packed film with a smooth surface. The band gaps of the MoO_x films with different x values were measured by light absorption measurement. Fig. 2c shows the $(Ah\nu)^{1/2}$ vs $(h\nu)$ curve, where A is the absorbance of a thin film, h and ν are the Planck constant and photon frequency. The value of band gap energy (E_g) was estimated from the intersection of the extrapolated linear part of the $(Ah\nu)^{1/2}$ curves with the photon energy axis. The E_g of $MoO_{2.86}$ was 2.82 eV, while that for MoO_3 was 3.24 eV. These values are consistent with the reported values by other researchers (Bouzidi et al., 2003; Greiner and Lu, 2013; Liu et al., 2013; Vasilopoulou et al., 2012; Werfel and Minni, 1983).

The CdTe work function variation upon the deposition of a MoO_x layer was quantitatively characterized by Kelvin probe force microscope (KPFM). In order to get reliable work function data, the KPFM comparative mapping image, shown in Fig. 3, was obtained on one substrate. Part of the CdTe film surface was covered by a cover during the MoO_x deposition and the other part of the uncovered CdTe film surface was deposited with a MoO_x film. Such an experimental design allowed us to obtain work function mappings of both the CdTe and the MoO_x on one sample. This avoided data acquisition uncertainty, which was induced by changing different samples during the KPFM measurement. Fig. 3a, show the KPFM work function mapping images obtained on CdTe surface and on the 5-nm-thcik $MoO_{2.86}$ on the CdTe film. It can be seen that upon the deposition of an $MoO_{2.86}$ oxide layer