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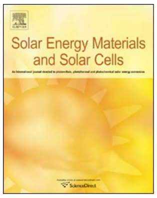

CdTe thin film solar cell with NiO as a back contact buffer layer

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ABSTRACT

In this work, p-type NiO thin film was applied as a buffer layer in the back contact for CdTe thin film solar cell fabrication. The NiO layers were prepared by electron beam evaporation. By optimizing NiO layer thickness in the back contact a CdTe solar cell with an efficiency of 12.17% and an open-circuit voltage V_{oc} of 790 mV has been fabricated. X-ray photoelectron spectroscopy study showed that NiO has a staggered band alignment with CdTe. Such an electronic band structure alignment allows smooth hole transport from CdTe to NiO and at the same time NiO acts as a surface field layer to reduce electron recombination at the back contact interface, thus leading to improved V_{oc}. This study also demonstrates that by employing NiO as a buffer layer, much less Cu was needed for the CdTe solar cell fabrication and the cell device stability had been significantly enhanced compared to the CdTe solar cell with a conventional Cu/Au bimetal layer as the back contact.

1. Introduction

CdTe is an outstanding II–VI material with a band gap energy of 1.45 eV and high light absorption (~10^5 cm^{-1}), which is much desired for fabricating high efficiency and low-cost photovoltaic devices [1–4]. In recent years, rapid progress has been made for the CdTe solar cell fabrication. The highest world-record efficiency has been increased from 16.7% to 22.1% in recent years, making the CdTe solar cell a strong competitive photovoltaic device to the market-dominant silicon solar cell [5,6]. In regarding to the fabrication of high efficient CdTe thin film solar cells, there are still some key issues to be understood and resolved. One of the problems encountered is a low-energy-barrier and stable contact fabricated on the CdTe surface. Due to the high work function of CdTe (~5.7 eV), and low p-type carrier density on the order of 10^{13}–10^{14} cm^{-3} in CdTe, it's a challenge to fabricate stable and low-resistance back contact CdTe solar cell [7,8]. Back contact structure using Cu is effective to make quasi-ohmic contact and improve the efficiency of CdTe solar cell. But copper is well known to diffuse easily from the contact region into CdTe and accumulate at the CdTe/CdS junction, resulting in device performance degradation over time [9–11]. To solve this problem, some researchers have focused on the usage of copper-free back contacts [12–14]. Some research groups have incorporated transition metal oxides (TMOs) as the buffer layer in the back contacts. The TMOs used include MoO_3 [15–17], V_2O_5 [18], and WO_3 [19], which have relatively high work function larger than ~6 eV. Paudel et al. have employed MoO_3 as back contact for CdS/CdTe thin film solar cell fabrication [15,19]. They found that the use of a MoO_3 buffer layer resulted in significant improvement of open-circuit voltage V_{oc}. A CdTe solar cell using MoO_3/Au back contact has reached an efficiency of 14.1%. Shen et al. have inserted V_2O_5 buffer layer in the back contact structure. They demonstrated that V_2O_5 layer could reduce the Schottky barrier at back contact and significantly improve the cell device stability [18]. All these reports employed n-type transition metal oxides. In this study we report CdTe solar cell fabrication by using p-type NiO as a buffer layer in the cell back contact.

NiO film is an oxide used widely in many fields, such as photovoltaic devices, LED, electrochromic devices and anti-ferromagnetic application [20–25]. In perovskite and polymer solar cells, several groups have applied NiO film as a hole transport layer (HTL) [20,26]. Recently, Jung et al. used NiO as hole contact for perovskite solar cell fabrication, and the cell efficiency was improved to 17.74% [20]. We suggest that NiO thin film may be an outstanding buffer layer for hole collection in the CdTe solar cell. In this study, we prepare NiO thin films by electron beam evaporation, and demonstrate that the insertion of p-type NiO buffer layer in the back contact can improve the CdTe solar cell open-circuit voltage, solar cell efficiency and cell device stability.

2. Experimental details

The CdTe solar cells fabricated in this study had a structure of glass/SnO_2:F(FTO)/n-CdS:O/p-CdTe/back contact/electrode. An intrinsic tin oxide interlayer was not introduced between the front electrode FTO

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and the window CdS layer. The n-type CdS films with a thickness of ~80 nm were prepared on glass/FTO substrates by RF magnetron sputtering at a substrate temperature of 200 °C. During the CdS sputtering, the RF power was 60 W, the chamber gas was 1% by volume for oxygen to argon, and the working pressure was 1.1 Pa. After heat treated in a $CdCl_2$ atmosphere, high quality crystalline CdS thin film with a monolayer of CdS grains was fabricated [27]. The CdTe absorber films, which had a thickness of 4–5 µm, were deposited by the close-spaced sublimation technique (CSS) in a home-made film deposition system. Subsequently, the CdS/CdTe stacked structures were activated with the presence of $CdCl_2$ in the dry air atmosphere to release interfacial strain and facilitate sulfur and tellurium mixing reaction at the CdS/CdTe interface [28]. Before back contact film deposition, the CdTe surface was chemically etched in a nitric-phosphoric solution (NP) for all the solar cells in this study. In order to investigate the effect of NiO buffer layer on cell device performance, solar cells with different back contact structures were fabricated, including Au-only, NiO/Au, Cu/Au, and Cu/NiO/Au multi-layer back contact structures. The NiO buffer layers were deposited by the electron beam evaporation technique in an ultra-high vacuum film deposition system. Films with thicknesses ranging from 5 to 40 nm were deposited at room temperature. The metal layers, namely, Cu, Au, and bilayer Cu/Au were deposited by thermal evaporation in a vacuum chamber. The solar cell size was 0.20 cm^2.

X-ray photoelectron spectroscopy (XPS) measurements were performed on 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 peak (284.60 eV). Solar cell current–voltage (J–V) curves were measured under standard AM 1.5 illumination (1 kW/m^2, 25 °C) using a solar simulator (Oriel Sol 3A, USA).

3. Results and discussion

Fig. 1(a) shows the atomic force microscope (AFM) image of a 200-nm-thick NiO film. The as-deposited NiO film is uniform and smooth, and the root-mean-square surface roughness obtained from AFM data is 0.99 nm. The X-ray diffraction (XRD) peaks at 37.2° and 62.8°, shown in Fig. 1(b), can be indexed as the (111) and the (220) atomic plane of cubic NiO phase (JCPDS 4-0835). The XRD pattern shows a strong (111) reflection and a weak (220) reflection. The NiO grain size was estimated to be ~28 nm calculated by using the Scherrer formula. The optical property of the NiO films was studied by light absorption measurement. Fig. 1(c) shows the plot of $(\alpha h\nu)^2$ versus $h\nu$, where α is the absorption coefficient obtained from light absorption measurement, h is Planck constant, and ν is photon frequency. We measured the band gap according the equation, $\alpha h\nu = A(h\nu - E_g)^{1/2}$, where A is a parameter related to the electronic band structure, carrier effective mass and the refractive index of the material, E_g is the band gap energy. The band gap of the as-grown NiO film measured in this study is 3.61 eV, which is in agreement with the reported values of 3.4–3.8 eV for the NiO [29–32].

The chemical states/compositions of the elements Ni and O in the NiO film were investigated by using XPS measurement. Fig. 2 shows the XPS spectra of the Ni 2p and the O 1s core level, respectively. The spectra were fitted with mixed Lorentzian-Gaussian curves. In Fig. 2(a), the Ni $2p_{3/2}$ XPS spectrum can be fitted into three component peaks. The peak centered at a binding energy of 853.9 eV corresponds to the Ni^{2+} states. The peak at 855.4 eV is ascribed to the Ni^{3+} state, which was induced by the presence of Ni^{2+} vacancy. The peak centered at 856.7 eV was related to the chemical shift due to the film surface absorption. These values are in good agreement with the reported binding energies for the relevant states in the literatures [23,33,34]. For the O 1s XPS spectrum the peaks located at 529.7 and 531.2 eV correspond to the Ni^{2+} and the Ni^{3+} state, respectively. The peak centered at 532.3 eV is related to surface absorption [35,36]. Therefore, in this study, the prepared NiO is non-stoichiometric, and the non-stoichiometry led the NiO material to be p-type semiconductor, which is desired for CdTe solar cell back contact fabrication [22,33].

The band alignment at the CdTe/NiO interface is vital for hole transport and formation of low electronic resistance contact. Desired band alignment can enhance hole transport and reduce carrier recombination at the back contact. Thus the open-circuit voltage may be enhanced. XPS technique was carried out to characterize the band alignment at the CdTe/NiO interface. XPS technique has been proved to be a direct and powerful tool for measuring valence band offset (ΔE_{VBO}) and conduction band offset (ΔE_{CBO}) at a hetero-structure interface [37,38]. The valence band offset ΔE_{VBO} at the NiO/CdTe interface can be calculated based on the following formula,

$$\Delta E_{VBO} = (Ni2p_{3/2} - E_{VBM})_{bulkNiO} - (Cd3d_{5/2} - E_{VBM})_{bulkCdTe} - (Ni2p_{3/2} - Cd3d_{5/2})_{interface}$$

where, $(Ni2p_{3/2} - E_{VBM})_{bulkNiO}$ and $(Cd3d_{5/2} - E_{VBM})_{bulkCdTe}$ are the energy difference between the $Ni2p_{3/2}/Cd3d_{5/2}$ core level and the valence band maximum measured on a thick NiO or CdTe film, respectively. The thickness of the XPS 'bulk' NiO and CdTe films were 200 nm and 4 µm. The XPS spectra and the corresponding values are shown in Fig. 3(a) and (b). $(Ni2p_{3/2} - Cd3d_{5/2})_{interface}$ is the energy difference between the $Ni2p_{3/2}$ and the $Cd3d_{5/2}$ core levels, which is to be measured at the NiO/CdTe interface. The coating layer of NiO must be thin enough to allow photon electrons to escape from the underlying CdTe film during the XPS measurement. In this study the coating NiO layer was 3 nm thick. The XPS spectra and the difference of these two core levels are shown in Fig. 3(c). From these values mentioned above the calculated valence band offset E_{VBO} at the NiO/CdTe interface is 0.52 eV. The valence band maximum of NiO is higher than that of CdTe. This is advantageous to hole transport from CdTe to the back contact. The conduction band offset ΔE_{CBO} at the NiO/CdTe interface can be obtained by using the equation, $\Delta E_{CBO} = \Delta E_{VBO} + E_{gNiO} - E_{gCdTe}$, where E_{gNiO} and E_{gCdTe} are the band gap values of NiO and CdTe. The E_{gNiO} is 3.61 eV, which was obtained from the UV absorption as shown in Fig. 1(c). The E_{gCdTe} is 1.45 eV. The ΔE_{CBO} calculated is 2.68 eV. Based on the XPS data, the quantitative electronic band alignment at the interface of CdTe/NiO/Au can be obtained and is shown in Fig. 4. The

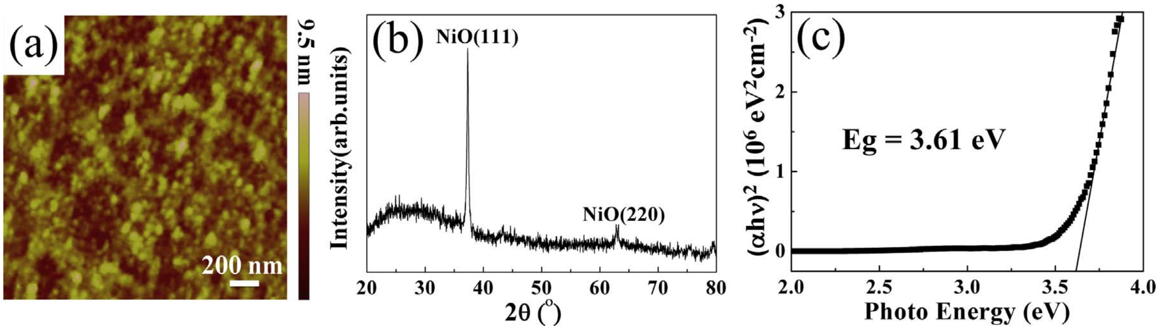

Fig. 1. (a) AFM surface morphology of a 200-nm-thick NiO film; (b) X-ray spectrum of the NiO film; and (c) $(\alpha h\nu)^{1/2}$ versus photo energy $h\nu$ obtained by light absorption measurement of a 200-nm-thick NiO film on glass.