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Band alignment of Cd-free (Zn, Mg)O layer with $Cu_2ZnSn(S,Se)_4$ and its effect on the photovoltaic properties

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ABSTRACT

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) is an interesting absorber material for thin film solar cells. However, one of the key challenges for the kesterite-based solar cells is to improve the open-circuit voltage (V_{oc}) deficit, which is resultant of recombination at the interface of buffer/absorber. In this work, Cd-free *n*-type buffer layers with two different Mg-doped ZnO layers ($Mg_{0.26}Zn_{0.74}O$, $Mg_{0.30}Zn_{0.70}O$) have been examined using ultraviolet photoelectron spectroscopy. The most important electronic properties which are essential for the band offset study, ie. fermi level location, valence and conduction band offsets at the interface in the CZTSSe substrate, have been determined. The conduction band offset values for $Mg_{0.26}Zn_{0.74}O$, $Mg_{0.30}Zn_{0.70}O$ buffer layers has been calculated experimentally. We have also established the correlation between device parameters and performances for dual ion beam sputtered ZnO buffer/CZTSSe-based heterojunction solar cells as a function of conduction band offset and the energy distribution of interface defects, to gain deeper understanding about the V_{oc}-deficit behavior from a high recombination rate at the buffer/kesterite interface using simulation study. From the simulation study, the values of the solar cell efficiency with $Mg_{0.26}Zn_{0.74}O$ and $Mg_{0.30}Zn_{0.70}O$ buffer layers are 10.18 and 10.25%, respectively, which are higher in comparison to those obtained by using conventional CdS buffer layer.

1. Introduction

Kesterite, $Cu_2ZnSn(S_x,Se_{1-x})_4$, have emerged as one of the most promising absorber materials for thin-film solar cells due to their low toxicity, natural abundance, outstanding light absorption, and higher theoretical efficiency (η) [1–3]. Interestingly, the record efficiency of CZTSSe based solar cells have reached 12.6% [4]. However, the η achieved for kesterite-based solar cell is quite less in comparison to thin film solar cells such as Cu(In,Ga) $(S,Se)_2$ (CIGS) (η = 22.6%) and CdTe (η = 22.1%), even though CZTSSe based solar cells have higher theoretical efficiencies (CZTSe: 31.0% and CZTS: 32.4% under single junction conditions) [5–7]. Further the efficiency of solar cells can be improved by incorporating plasmons [8–12]. A major hindrance to the efficiency of CZTSSe based solar cells is the open-circuit voltage deficit (Voc-deficit: $E_g/q–V_{oc}$, where E_g is the bandgap energy of the kesterite and q is the electron charge), which results from a non-optimized conduction band offset (CBO) between the CZTSSe absorber and the buffer layer [13,14]. As a kesterite absorber material, CZTSSe is derived from chalcopyrite CIGS, so the device structure of CZTSSe based solar cells have been adopted from CIGS-based solar cells, where CdS is used as a conventional buffer layer [15–17]. However, CdS buffer layer has some drawbacks: (1) Due to lower bandgap (2.4 eV) of CdS, the short wavelength light is absorbed which reduces the short circuit current density (J_{sc}). Furthermore, if the bandgap of the CZTSSe absorber varies, the subsequent bandgap variation is not possible in CdS. Therefore, the conduction band alignment of the CdS/CZTSSe interface turns inappropriate; and (2) Cd is toxic, so it is essential to substitute it with a more environmentally promising material. The buffer layer material whose bandgap can be controlled, such as Mg-doped ZnO (MZO) and Zn(O,S), are being explored [18–21]. However, there are only a few studies on buffer layers as the replacements to CdS in CZTSSe based solar cells [22]. Here, MZO material is chosen because of its cost

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effectiveness and non-toxicity while realizing an environmentally benign solar cell [23–25].

In this study, we have performed an analysis to improve CZTSSe-based solar cell performance by enhancing the short-wavelength response and optimizing conduction band offset of dual ion beam sputtering (DIBS) grown MZO/CZTSSe heterojunction. We have also systematically demonstrated the deeper insight and understanding on CBO and recombination behavior resulting from the interface at the buffer/absorber through the study on the relationship between device performances and parameters of CZTSSe-based thin film solar cell. A comparative analysis of CBO for different Mg content in MZO has been performed using ultraviolet photoelectron spectroscopy (UPS). Spectroscopic ellipsometry (SE) measurement has been performed on MZO and CZTSSe films to evaluate the optical parameters. The influence of CBO and interface recombination are quantified by device simulations. To the best of our knowledge, there are no reports available in the literature regarding a detailed study of band alignment parameters at the interface of *n*-type MZO and *p*-type CZTSSe grown by DIBS system.

2. Experimental details

Deploying the Elettrorava DIBS system, a) 150 nm thick $Mg_{0.26}Zn_{0.74}O$ (MZ1) and $Mg_{0.30}Zn_{0.70}O$ (MZ2) thin films are deposited on glass substrates at 200 °C, and b) 150 nm thick CZTSSe thin films are deposited on glass substrates at 300 °C, the details of which is explained elsewhere [26]. The deposition of the individual thin film has been carried out in Ar atmosphere with a chamber working pressure of 2.4×10^{-4} mbar and ion beam power of 45 W. A 5-nm layer of MZ1 and MZ2 is grown on 150 nm of CZTSSe film on glass to prepare MZ1/CZTSSe and MZ2/CZTSSe heterojunctions, respectively. UPS measurement has been carried out by utilizing the angle-integrated photoelectron spectroscopy system (AIPES) in the beam line of the INDUS-1 synchrotron source. The background pressure inside the AIPES experimental chamber is maintained at $\sim 2 \times 10^{-9}$ mbar. During UPS measurement, to remove the adsorbate from the surface, the sample surface has been carefully cleaned by short and mild Ar + ion beam of energy 500 eV for 5 min at 2.66×10^{-5} mbar at room temperature, in the preparation chamber, which is disconnected by a gate valve from the AIPES chamber. After that, thin films has been moved to the experimental chamber, and UPS spectra has been measured after the sputtering process. The incident photon energy, photoelectron counts steps, and pass energy are 100 eV, 0.02 eV, and 20 eV respectively for the measurement. Polycrystalline Au foil is transferred into the chamber with CZTSSe, MZ1, and MZ2 samples. The UPS measurement performed on Au foil is utilized as a reference signal to illustrate the monochromatic synchrotron emission and the Fermi energy level (E_F) of the metallic sample holder. The optical properties of MZ1/CZTSSe and MZ2/CZTSSe heterojunctions, optical functions (refractive index (n), and extinction coefficient (k)), thickness and roughness of CZTSSe, MZ1, and MZ2 thin films has been measured using M-2000D J. A. Woollam variable angle SE. Photoluminescence (PL) measurements are performed on MZ1, and MZ2 thin films using a PL set-up equipped with a 20 mW continuous wave He−Cd laser as excitation source. The chemical composition of MZO thin films has been measured by energy dispersive X-ray spectroscopy (EDX, Oxford Instruments). Four-probe Hall measurement setup is employed to evaluate the electrical properties of CZTSSe and MZO thin films.

3. Results and discussion

3.1. Optoelectronic properties

SE is a non-invasive and non-destructive technique, which is used to obtain optical constants through the analysis of the complex dielectric function. SE measurement gives the spectral variation of the two ellipsometric angles, Ψ, and Δ, as given in equation (1):

$$\rho = \frac{r_p}{r_s} = \tan\Psi e^{i\Delta} \tag{1}$$

where r_p and r_s are the amplitude reflection coefficients for p- and s-polarized light waves, respectively, Ψ is the ratio of the amplitude reflection coefficients, and Δ is the phase difference between s- and p-polarized light waves.

It is prominent phenomena that the SE technique is very sensitive to the surface roughness of a thin film. Therefore, in order to account for this surface roughness, the Bruggeman effective medium approximation (EMA) [27] is applied to the top stack layer. In this article, the SE investigation is constructed on a three-phase model, i.e., air/surface-roughness layer/thin film/substrate. The EMA model, in general, is based on equation (2) [27]:

$$\frac{\varepsilon_{thin\ film} - \varepsilon_i}{\varepsilon_{thin\ film} + 2\varepsilon_i} f_v + \frac{\varepsilon_{air} - \varepsilon_i}{\varepsilon_{air} + 2\varepsilon_i}(1 - f_v) = 0 \tag{2}$$

where ε_i is the effective complex dielectric function of the surface-roughness layer, f_v is the volume fraction of thin film in the surface-roughness layer and the value is fixed to 50%, ε_{air} is the dielectric constant of air ($\varepsilon_{air} = 1$ assumed in all SE analysis), and $\varepsilon_{thin\ film}$ is the complex dielectric function of thin film. All ellipsometric measurements are performed with an incidence angle of 70° in the wavelength range of 190–1000 nm. The measured data is fitted by Tauc-Lorentz model [28] using Complete EASE software [29] and the model shows good agreement with the experimentally obtained data in the whole spectral range. Fig. 1(a) demonstrates experimentally measured and fitted spectra of the ellipsometry angles, ψ and Δ, of MZ1 and MZ2 films deposited by DIBS. Fig. 1(a) illustrates the oscillation patterns below photon energy 3.7 eV, which are essentially thickness fringes as a result of the transparent characteristic of films below their optical absorption edge.

It can be observed from Fig. 1(a), no interference oscillation is perceived above photon energy 3.7 eV, as a result of light absorption resulting from the inter-band transition in both MZ1 and MZ2 films. The transmission spectra of MZ1 and MZ2 thin films grown on a glass substrate are shown in Fig. 1(b)–(c), respectively. The bare substrate is used as a baseline for all the samples. The optical absorption coefficient (α) is determined from the measured spectral transmittance (T_λ) and reflectance (R_λ) using equation (3):

$$\alpha t = \ln\left[\frac{(1 - R_\lambda)^2}{T_\lambda}\right] \tag{3}$$

where t is the film thickness. The insets of Fig. 1(b) and (c) show the $(\alpha h\nu)^2$ vs. $h\nu$ plots, by which the bandgaps of MZ1 and MZ2 are evaluated. The bandgaps of MZ1 and MZ2 films are 3.90 and 3.94 eV, respectively. These bandgap values are also determined from the fitting of various modeling parameter of ellipsometric data using the Tauc-Lorentz oscillator which is well matches with bandgap calculated using transmittance. The optical constants n and k of MZ1 and MZ2 thin films, as calculated from SE data, are depicted in Fig. 1(d) and (e). We observed that MZ1 and MZ2 films show a high refractive index (n = 1.68–2.02) in the ultraviolet (UV)–visible region additionally the fundamental absorption edge in the near-UV region. The n values initially increase as energy increases till 5.2 eV and then decreases with the energy increases from 5.2 to 6.4 eV, that is compatible with Kramers–Kronig relations [30]. The extinction coefficient (k) value increases as energy increases while k values are zero at lower photon energies, which indicates that the films are transparent in this range.

Fig. 1(f) shows the room-temperature PL spectra of MZ1 and MZ2 thin films. PL spectra displays the presence of a UV band located at 331 nm. It can be observed that the PL peak position shows a blue shift as Mg composition increases from MZ1 to MZ2. As depicted in Fig. 1(f), the linewidth of PL peak of MZ2 is broader in comparison to that of MZ1. This PL peak broadening shows inhomogeneous alloy broadening