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Effect of Zn(O,S) buffer layer thickness on Charge carrier relaxation
dynamics of CuInSe₂ solar cell

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Abstract

A pinhole free Zn (O S) buffer layer was deposited on CuInSe₂ (CIS) absorber by chemical bath deposition (CBD) method. Thin Zn(O,S) exhibits better power conversion efficiency (PCE) at lower thickness. Enhancement of PCE from 1.5% to 3.9% was observed for electrodeposited CIS photovoltaic device when the buffer layer thickness reduces from 50nm to 20nm. Although the conduction band offset (CBO) at Zn(O,S)/CIS interface are almost identical for both the 20nm and 50nm thick buffer layers, investigation on charge carrier dynamics reveals that the carrier lifetime for the 20nm buffer is much longer than the 50nm buffer. This offers a plausible explanation for the higher J_{sc} of the device with 20nm buffer layer compared to the device with 50nm buffer layer.

Key words: Solar cell, CuInSe₂, Buffer layer, Zn(O,S), Pump-Probe, charge carrier dynamics,

1. Introduction

There has been considerable research interest for high efficiency CuInGaSe₂ (CIGS) based thin film solar cells because of promising material properties and outstanding performance. A variety of methods are used today for the fabrication of such cells and currently, the highest cell efficiency is reported as 21.7% (Jackson et al., 2015). Most of these cells are obtained using CdS buffer layer deposited by chemical bath deposition (CBD). However, there are some debates on the fundamental issues with this buffer layer, mainly because of the toxicity of Cd and the non-ideal band gap. CdS has band gap energy about 2.4-2.5 eV, which is non-optimal for cell performance especially in the short wavelength domain as it has considerable absorbance in these regions (Siebentritt, 2004 and Hariskos et al., 2005). Hence, many research efforts in the realm of CIGS solar cells are focused on the development and implementation of Cd-free alternative buffer layer (Naghavi et al., 2010 and Lee et al., 2014)

To find out the best candidate many alternative materials have been tested in the past decade for a Cd-free buffer layer (Siebentritt, 2004, Cherian et al. 2012) in CIGS solar cells. ZnS-based buffer layer has emerged to be one of the most promising candidates for this purpose (Kushiya et al. 1996, Kushiya, 2004, Shin et al. 2011, Bhattacharya et al. 2004). There are few reports to develop the ZnS based buffer layer as a promising alternative of CdS based buffer layer (Merdes et al. 2014, Kushiya et al. 1996, Nakamura et al. 2013, Spiering et al. 2006). It was reported that CIGS cells fabricated with chemical bath deposited (CBD) Zn-S buffer layer yielded 19.7% efficiency (Nakamura et al., 2013) , comparable to the efficiency of CIGS cell with CdS buffer which was used as a control in that study. Initially very thick Zn(O,S) buffer layer were used,

such as 120nm Zn(O,S) achieved by 3 cycles of CBD deposition (Nakada et al., 2001, Bhattacharya et al. 2004), Japanese CIGS manufacturing company showa Shell (Hariskos et al., 2005) deposited a Zn(O,S) buffer with a thickness of around 50nm. While there were differences in the deposition methods used by the various groups, it is noted that most of the research groups used a Zn(O,S) buffer of about 50-100nm (Nakada et al., 2001, Contreras et al., 2003 and Hsieh et al., 2014). Recently, Very thin CBD grown Zn(O,S) buffer layer was reported as highly promising buffer layer (Kobayashi et al., 2013, Nguyen et al. 2014). This result was also echoed by reports from other research group (Wei-Tse et al., 2012) who compared the 15nm CBD-Zn(O,S) with the control 50nm CdS buffer layer for CIGS solar cell applications. The excellent performance of ultra thin Zn(O,S) buffers were reported either by CBD (Kobayashi et al., 2013 and Wei-Tse et al., 2012) method or the atomic layer deposition (ALD) (Platzer-Björkman et al., 2006 and Uhm et al., 2014). However, the results are largely empirical and the fundamental science to explain the reasons for the equivalent or better performance of the ultra thin buffer layer compared to the thicker one is still unclear.

Here we aim to understand the effect of thickness of Zn(O,S) buffer layer on CIS solar cell. The optical properties and PCE of CIS solar cells with different thicknesses of Zn(O,S) buffer layers were investigated. Details stoichiometries of the buffer layer were studied when the thickness increases by XPS analysis which helps to understand the charge carrier dynamics of the buffer layer for different thickness. We want to investigate how the thickness of the buffer layer effected the Jsc of the photovoltaic device depends on the buffer layer deposition condition and how the carrier life time in the buffer layer is depends on the thickness of the buffer layer. Although there were few reports on the utilization and optimization of Zn(O,S) buffer layer for

CIGS solar cell, this paper is the first to correlate device data to charge carrier dynamics and investigate the effect of thickness of the buffer layer by optical probing.

2. Experimental

2.1 Materials

In order to prepare the deposition bath, Zinc acetate dihydrate (Sigma Aldrich, ACS reagent grade, $\geq 98\%$), Thiourea (Sigma Aldrich, ACS reagent grade, 99%) and Ammonia hydroxide (Sigma Aldrich, ACS reagent grade, 28-30%) were used as received without further purification.

2.2 Thin film growth and device fabrication

To study the optical properties of Zn(O,S) film, the film was deposited onto plasma cleaned UV-transparent quartz substrate by a CBD method. The chemical bath solution was comprised of 0.08M Zn (Ac)₂, 5M Thiourea (TU) and 7M NH₃ in deionized (DI) water. Zn (Ac)₂ powder was first added into DI water then followed by TU powder. When the temperature of water bath reached close to 85°C, concentrated NH₃ was added. The whole bottle of mixed precursor solution was placed into the water bath with stirring. And then the reaction started. The pH of the solution was maintained between 10 and 11. The NH₃ produced from the NH₄OH worked as a complexing agent to form complexation with Zn²⁺ and then control the growth of ZnS, through following reactions (Shin et al., 2013).

Complexation process:

ZnS film growth

Because the solution is basic, $\text{Zn}(\text{OH})_2$ will also form through

The deposition time was varied from 12mins and 25mins to vary the thickness of $\text{Zn}(\text{O,S})$ film.

The quartz substrate was then taken out from the chemical bath and washed in NH_3 solution (aqueous 2.5% solution) in order to clean out the uncontrollable precipitation of $\text{Zn}(\text{OH})_2$ on the surface. At last, the quartz substrate was rinsed with DI water and dried under N_2 gun. Then the films were annealed at 200°C for 20mins to convert $\text{Zn}(\text{OH})_2$ inside $\text{Zn}(\text{O,S})$ film to ZnO .

To fabricate the CIS solar cell, a 500nm-thick molybdenum (Mo) back contact was deposited by DC-magnetron sputtering on soda lime glass (SLG) substrates. To clarify the basic device structure a schematic representation of the device are provided in supporting information S1. The Elemental Cu and In were deposited onto Mo substrate sequentially by electrodeposition method (Calixto and Sebastian, 1998 and Bhattacharya, 2013). The Cu/In ratio was kept around 0.85. A layer of 1.5 μm -thick CIS was formed through the selenization of Cu and In metallic layer in tube furnace at 520°C . Then the $\text{Zn}(\text{O,S})$ buffer layer was deposited immediately onto CIS surface by immersing the CIS sample into the CBD deposition bath. Different thicknesses of $\text{Zn}(\text{O,S})$ were deposited onto CIS by varying the deposition time. After $\text{Zn}(\text{O,S})/\text{CIS}$ were deposited, washed, rinsed, dried and annealed at 200°C for 20mins. After buffer layer deposition the device fabrication was completed by sputtering the transparent conducting oxide (TCO) layer and finally putting the front contact metal electrode following our standard procedure (Ho et al. 2014). Typically 500 nm intrinsic-ZnO (i-ZnO)/aluminium doped zinc oxide (AZO) deposited by sputtering followed by evaporation of 3 μm thick Ni/Al grid front contact electrodes.

2.3 Film and device characterization

The optical properties of Zn(O,S) film on quartz substrate were measured by Ultraviolet-Visible (UV-Vis) spectroscopy. The planar and cross-section images of Zn(O,S)/CIS samples were obtained by Field Emission Scanning Electron Microscope (FESEM), JEOL JSM-7600F. The valence band offset at Zn(O,S)/CIS was measured by XPS depth profile. In order to study the ultrafast carrier relaxation dynamics in CIS films, femtosecond optical pump-optical probe (OPOP) measurement was carried out. Second harmonic generation (SHG) of fundamental 800 nm (400 nm) wavelength was used as pump; and beam from optical parametric amplifier (OPA) used as probe. Differential probe signals were collected using photodiode and lock-in amplifier, with respect to pump delay. In this experiment, the pump and probe pulses were orthogonally polarized with the incident angle between both the beams less than three degrees. The ratio of energy between the pump and the probe pulses was less than 5%.

The transient optical properties of the interface were also measured by time resolved photoluminescence. OPA was pumped by an amplified-femtosecond pulsed laser system (Spectra physics, Mai Tai-Spitfire Ace-TOPAS Prime). The output wavelength can be continuously tuned from 250 nm to 2.6 μm . The pulse-width and repetition rate are 100fs and 1 KHz, respectively. The Zn(O,S) film samples were excited at a wavelength of 325 nm, beam spot size 3 mm. The photoluminescence (PL) signals from the sample were dispersed by a 3/4 m monochromator (Princeton instruments, adjusted to 550 nm) assisted with a pair of collection lenses and a long-pass filter (cut-off wavelength: 350 nm) and recorded by an Optronics streak camera system with time resolution of $\sim 50\text{ps}$ (Wang et al., 2014).

The current density-voltage (J-V) characteristics of devices (0.1cm^2 active area) were measured under a solar simulator in ambient conditions under AM 1.5G illumination ($100\text{mW}/\text{cm}^2$) using a Keithley SMU 2400 source meter. The light intensity was calibrated by using an NREL calibrated silicon photodiode. The external quantum efficiency (EQE) was measured using a PVE300 (Bentham), with dual Xenon/quartz halogen light source, measured in DC mode.

3. Results and Discussions

Fig. 1a shows the top-view FE-SEM image of Zn(O,S) grown on selenized CIS. The Zn(O,S) film shows excellent coverage on CIS without pinholes. Fig. 1b shows the XPS surface scan of the Zn(O,S)/CIS surface with different Zn(O,S) thickness. We can observe all peaks from Zn, S and O, and there are no peaks corresponding to Cu, In and Se, even for the 20nm Zn(O,S)/CIS samples. This further confirms that the coverage of the Zn(O,S) on CIS film is uniform and conformal. The as deposited films are amorphous in nature as observed from XRD (supporting information S2) analysis but after annealing small peaks are observed, which are identical to ZnS with small shift because of oxygen inclusion.

The cross section FESEM images of Zn(O,S)/CIS interface of two different CBD conditions are shown in Fig 1c and 1d. In our deposition process, 12mins deposition resulted in around 20-25 nm Zn(O,S) (Fig. 1c), and 25mins deposition produced a layer of 50 nm Zn(O,S) (Fig. 1d).

Fig.1 (a) Planar FE-SEM image of annealed Zn(O,S) on top of CIS, (b) XPS survey scan for the surface of Zn(O,S)/CIS/Mo, and cross section of Zn(O,S)/CIS interface with (c) 20nm Zn(O,S)/CIS,(d) 50nm Zn(O,S)/CIS

Fig. 2a shows the optical absorption spectra of the Zn(O,S) layer deposited on UV-transparent quartz after annealing at 200°C for 20mins. The Zn(O,S) film was characterized under UV-Vis spectroscopy at a wavelength range of 300-800nm. We can see from Fig. 2a that the transmittance of 50nm film is slightly lower than that of 20nm film at the 300-600nm range. The band gap of the 20nm Zn(O,S) is estimated from the absorption edge as 3.75 eV. After increasing the CBD time, the film thickness increases to 50 nm, and the optical absorption properties changes. The average band gap for 50nm film decreases to 3.4 eV. The reason for this decrease is due to the dependence of the E_g of Zn(O,S) on the S/(S+O) ratio (Meyer et al., 2004 and Persson et al., 2006). M.bar.et al reported that when CBD method was used for buffer layer deposition, S/(S+O) ratio is thickness dependent, thus creating a compositionally-graded

ZnS/(ZnS+ZnO) layer (Bär et al., 2006). At the initial growth stage, a very thin ZnS film is formed and at the later growth stage, more O is incorporated in the ZnS film, resulting in a decreased S/(S+O) ratio. Fig. 2b shows the XPS depth profile of 50nm Zn(O,S)/CIS from the Zn(O,S) surface to the Zn(O,S)/CIS interface with increasing sputtering time. It is observed that, the S/(S+O) ratio increases gradually from around 0.5 on the surface of Zn(O,S) (0s sputtering) to 0.7 at the Zn(O,S)/CIS interface (400s sputtering). Due to the characteristic growth process of CBD-Zn(O,S), (as discussed in supporting information S3) (Shin et al., 2013) we can assume that the composition profile from 240s sputtering onwards is quite similar to that of 20nm Zn(O,S), provided constant sputtering rate and Zn(O,S) growth rate. Since the S/(S+O) has a direct impact on E_g , (Meyer et al., 2004) (Persson et al., 2006), it can be inferred that the average band gap of these two films should vary according to the stoichiometry. The average band gap for the sulfur rich 20nm Zn(O,S) estimated from absorption onset is 3.75 eV. This band gap value is close to that of pure ZnS film (3.8 eV); while for the 50nm film, the estimated average band gap is closer to the theoretical band gap of ZnO (3.2eV).

Fig.2 (a) optical transmittance of Zn(O,S) film grown on quartz substrate for different time with annealing treatment at 200°C for 20mins, (b) XPS depth profile for a sputtered 50nm Zn(O,S)/CIS layer.

A series of device were tested with 20nm and 50nm thick Zn(O,S) buffer layer after post treatment at 200°C in air for 20mins and all the parameter are tabulated in table 1 for comparison. The value for J_{sc}, Voc and FF decrease on changing the buffer layer from 20nm to 50nm so the device efficiency also decreases from 3.2±0.60 % to 1.5±0.04%.

Table 1: Parameter for J-V characteristics of photovoltaic device with 20nm and 50nm thick Zn(O,S) buffer layer:

Buffer Layer Thickness (nm)	Voc (V)	Jsc (mA/cm ²)	Fill Factor (%)	Efficiency (%)
20 nm	0.285±0.017	34.25±7.44	33.14±3.91	3.20±0.60
50 nm	0.233±0.035	20.39±3.05	32.03±1.51	1.50±0.04

Figures 3a and 3b show the J-V curves and external quantum efficiency (EQE) spectra of the champion device. As shown in Fig. 3a, the cell with 20nm Zn(O,S) has a power conversion efficiency of 3.9%. When the buffer thickness is increased to 50nm, there is small decrease in V_{oc} and FF values. Also the J_{sc} decreases sharply from 38.8mA/cm² to 16.6mA/cm², resulting in a decline in PCE to 1.53%. Here the observed PCE of our device is very low in comparison to the reported high efficiency CIGS device (21.7%) (Jackson et al., 2015). As our absorber layer is not optimized observed Voc and Fill Factor is less than the half of the reported value for highest efficient device.

Fig. 3b shows that the EQE of the champion cell, the EQE of 50nm cell is only about half of the EQE of 20nm cell for the entire wavelength range measured. The integrated photocurrent measured by EQE is consistent with J_{sc} whereby the J_{sc} of 50nm cell is also about half of that of 20nm cell. There is slight difference on the onset of the absorbance of the device in EQE curve

on higher wavelength region. Probably, different degrees of selenization in the different position of selenization tube developed slight different band gap of the absorber. Series resistance and shunt conductance of the device were calculated from the J-V curve by the curve fitting method with the help of the Lambert W function as described by Zhang et al. (Zhang et al., 2011). Details of the extracted device parameters are now described in the supporting information (supporting information S4). The series resistance and shunt conductance of the device with 20nm buffer layer were found as 1.908 Ohm cm^2 and 59.4 mS/cm^2 where as these values for the device with 50nm buffer layer were found as 1.945 Ohm cm^2 and 15.6 mS/cm^2 respectively. The obtained shunt conductance value is quite high for our device probably because of the non-optimized absorber layer. We also tried to fabricate the device with thinner buffer layer of 10nm Zn(O,S) layer, but it did not work. A probable reason is the coating was not conformal enough and sputtered ZnO layer make direct contact with the absorber layer (supporting information S5).

Fig.3 (a) J-V curve and (b) EQE spectra of CIS solar cell fabricated with 20nm and 50nm Zn(O,S) annealed at 200°C for 20mins.

The band alignment of the heterojunction is determined from depth profiling XPS of shallow core levels and the valence band edge as shown in Fig. 4a. During the depth profiling towards

the interface, the shallow core levels of Zn 3d and In 4d of the Zn(O,S) and CIS, respectively, are monitored. When the relative contribution of the shallow core levels are similar in intensities, the level of depth profile is taken to indicate the Zn(O,S)/CIS interface where the valence band offset (VBO) measurement is obtained. However, since this interface spectrum contains overlapping valence band contribution from each material, they have to be deconvoluted to avoid errors associated with overlap of valence band signals (Chiam et al., 2008). In this approach, we use the bulk valence band spectra of sputter clean Zn(O,S) and CIS at the interface, as shown in Fig. 4b respectively, to achieve the deconvolution. The shallow core levels of the bulk materials are scaled to match both the intensity and the binding energies as measured from the interface spectrum. This will account for both electrostatic and intensity variations. The scaled bulk spectra were subsequently summed to check the agreement with the interface spectra and this is shown in Fig. 4c, where a good agreement was observed. The VBO can then be determined from the individual bulk valence band edges after the scaling and alignment as shown in Fig. 4a. A VBO value of 1.2 eV is obtained for the Zn(O,S)/CIS interface. (4) The corresponding CBO can be derived from the equation

$$\text{CBO} = E_g \text{ Zn(O,S)} - E_g \text{ CIS} - \text{VBO} \text{ (Nakada et al., 2003 and Lee et al., 2012)}$$

Fig. 4d shows the XPS survey spectrum of the bare CIS surface with the individual elements. The composition of the film is determined from quantitative analysis of the fitted core levels from the individual elements. This yields a material composition of $\text{CuIn}_{2.9}\text{Se}_{4.8}$. This stoichiometry is close to that reported for surface composition of CIS (CuIn_3Se_5), where an ordered vacancy compound (OVC) exists and this yields a band gap of 1.23 eV and this is the value used for our CBO calculation (Negami et al., 1995). As the initial growth of 50nm Zn(O,S) and 20nm Zn(O,S) are from identical deposition bath, so it is quite obvious that the composition

of both the buffer is quite identical at the interface, hence we have used the band gap value (3.75eV) of 20nm Zn(O,S) for CBO calculations. According to equation (4), the calculated CBO value is 1.32 eV, which is very close to the reported value (Nakada et al., 2003).

Importantly, it is shown from this work that CBO value for the 20nm Zn(O,S)/CIS would be very similar to the CBO of 50 nm Zn(O,S)/CIS as the calculated VBOs and compositions of the material are similar. With the assumptions that the CBO values of 20nm and 50nm Zn(O,S)/CIS are similar, it also helps to explain the identical V_{oc} of the devices since there is a direct correlation between the CBO and V_{oc} values (Kobayashi et al., 2013). We therefore conclude from our studies that the CBO in our devices is not the dominant factor that gives rise to the drastic performance differences as observed.

Fig.4 (a) XPS depth profile of 50nm Zn(O,S)/CIS interface (Top black curve of Zn3d peak signifies the surface profile and other colour curve towards the interface as represented by the

arrow), (b) XPS bulk profile of CIS and Zn(O,S), (c) interface spectra matching with scaled bulk spectra and (d) XPS surface scan of selenized CIS

In order to further investigate the fundamental reasons of the superior performance of 20nm Zn(O,S)/CIS cell compared to the 50nm Zn (O,S)/CIS cell, the carrier (electron) relaxation dynamics of CIS at the Zn(O,S)/CIS interface was investigated by femtosecond optical pump-optical probe (OPOP). The Zn(O,S)/CIS was pumped at 800nm, and then probed at 900nm. The decay curves of bare CIS and CIS/Zn(O,S) samples are shown in Fig. 5a. As the probe is at 900nm, this decay represents the decay of the carriers from CIS to the Zn(O,S) layer. It is observed that there is a delay in the excitation of 20nm Zn(O,S)/CIS and 50nm Zn(O,S)/CIS compared to bare CIS. This correlates to the rise time of these three different samples (Table 2). The rise time of 20nm Zn(O,S)/CIS and 50nm Zn(O,S)/CIS has both increased from 2ps (bare CIS) to 9ps (Zn(O,S)/CIS). Longer rise time indicates that the electrons take more time to saturate the conduction band of CIS. The delay in the saturation of CIS electrons in conduction band is evidence of charge transfer from CIS conduction band to the conduction band or defect states of Zn(O,S), which confirms that there is a charge transfer process between CIS and Zn(O,S) as shown in Fig.6 (process 2 &3). The electron decay time of these two samples are both higher than that of bare CIS sample. The electron decay time of CIS in the 20nm Zn(O,S)/CIS sample is much higher(43ps) than the 50nm Zn(O,S)/CIS sample (25.8ps), indicating that the recombination rate of 20nm Zn(O,S)/CIS in the depletion region is much slower than that of 50 nm Zn(O,S)/CIS. This is probably due to lower defect density in the 20nm Zn(O,S) film than the 50nm Zn(O,S) film. During the second half growth of 50nm Zn(O,S), more Zn(OH)₂ is formed.

After heat treatment, $\text{Zn}(\text{OH})_2$ is converted to ZnO , leaving behind a lot of dangling bonds. These dangling bonds are source of traps for the recombination of electrons and holes. Therefore, the charge relaxation time of 20nm $\text{Zn}(\text{O,S})$, is higher than that of 50nm $\text{Zn}(\text{O,S})/\text{CIS}$. In other words, the recombination rate of 20nm $\text{Zn}(\text{O,S})/\text{CIS}$ is much lower than that of 50nm $\text{Zn}(\text{O,S})/\text{CIS}$, which supports the higher J_{sc} value for the 20nm $\text{Zn}(\text{O,S})/\text{CIS}$ solar cell than that of 50nm $\text{Zn}(\text{O,S})/\text{CIS}$ solar cell.

Table 2: OPOP decay parameters and τ the lifetime and t the corresponding rise time

samples	Decay τ 1(ps)	Rise t (ps)
CIS	12 ± 3	2 ± 1
20nm $\text{Zn}(\text{O,S})/\text{CIS}$	43 ± 5	9 ± 2
50nm $\text{Zn}(\text{O,S})/\text{CIS}$	26 ± 5	9 ± 2

Femtosecond laser excited time-resolved photoluminescence (TRPL) decay curves of the $\text{Zn}(\text{O,S})/\text{CIS}/\text{glass}$ samples collected at defect states emission (550 nm) of $\text{Zn}(\text{O,S})$ are shown in Fig.5b. Best fits to the decay curves are achieved with double exponential decays. Decay times and their coefficients are tabulated in Table 3. The first decay is found to be little affected by changes in thickness of $\text{Zn}(\text{O,S})$ film, but second decay is longer for thinner $\text{Zn}(\text{O,S})$. The lower PL intensity for the 20 nm film than 50 nm proves that there are fewer defects in 20nm $\text{Zn}(\text{O,S})/\text{CIS}$ sample.

Fig.5 (a) pump probe transient for the Zn(O,S)/CIS/glass samples with 20nm and 50nm Zn(O,S) after heat treatment at 200 °C for 20mins. (b) Time-resolved luminescence decay curve. Excitation wavelength was 325nm.

Table 3: Luminescence decay parameters obtained with an excitation wavelength at 325 nm and τ the lifetime and A the corresponding amplitude

samples	A1	τ_1 (ps)	A2	τ_2 (ps)
20nmZn(O,S)/CIS	0.7 ± 0.02	190 ± 50	0.3 ± 0.02	2300 ± 150
50nmZn(O,S)/CIS	0.7 ± 0.02	170 ± 40	0.3 ± 0.02	1600 ± 100

The reason for the slightly faster decay time τ_1 could be due to surface defects at the Zn(O,S) surface. Surface defects results in a higher recombination rate of electrons and holes. After the CIS solar cell is irradiated under light, the holes will be transported to CIS side and conducted to circuit through Mo back electrode and the electrons from CIS will transport to buffer Zn(O,S) side then to TCO and conducted to circuit. Compared to the τ_2 life time of the 20nm Zn(O,S)/CIS (2294 ps), the τ_2 life time for the 50nm Zn(O,S) is much shorter (1570 ps). This is because the

fewer defects inside 20nm Zn(O,S). As the hydroxide moieties deposited inside the film in the later stage of deposition(as discussed in supporting information S3) (Shin et al., 2013), the thicker buffer layer contains more hydroxide group, The formation of Zn(OH)₂ at the later stage of the CBD growth causes a lot of dangling bonds in the Zn(O,S) film. These dangling bonds act as the defect centre for the solar cell. During photoexcitation, electrons and holes will be separated at the absorber/buffer interface and electrons will be transported to the buffer side. The defects in the buffer will affect the electron transport from CIS to Zn(O,S) and reduces the lifetime of these electrons. A higher rate of recombination is also another reason to explain why the life time for the 50nm Zn(O, S) is much reduced compared to 20nm Zn(O,S)/CIS and to explain why J_{sc} for the 50nm Zn(O,S)/CIS cell is only half of the J_{sc} of 20nm Zn(O,S)/CIS cell.

Fig.6. Band diagrams of Zn(O,S)/CIS/glass samples.

4. Conclusions

A uniform and pinhole-free Zn(O,S) film was deposited by CBD method on electrodeposited CIS film. The PCE for the cell with 20nm buffer is higher than that of 50nm buffer. This phenomenon is attributed to the higher defect density of the 50nm Zn(O,S) as shown by the

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4 pump probe and TRPL measurements. The carrier lifetime extracted by pump probe
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6 measurements for the electrons in 20nm Zn(O,S)/CIS is much higher than that of 50nm
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8 Zn(O,S)/CIS, which is consistent with and explains our finding that the J_{sc} of the 20nm Zn(O,
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10 S)/CIS cell is almost double that of 50nm Zn(O, S)/CIS cell.
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