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Optimized Electronic Structure of Cu(In,Ga)Se₂ Solar Cell with Atomic Layer Deposited Zn(O,S) Buffer Layer for the High Power Conversion Efficiency

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Abstract

To minimize carrier recombination at interfaces and maximize the open circuit voltage and resultant power conversion efficiency, it is imperative to characterize and optimize the heterointerfaces of Cu(In,Ga)Se₂ (CIGS) thin film solar cells. In this study, we investigated the surface chemical and electronic structure of CIGS with In-final and Ga-final co-evaporation processes and observed that the In-final CIGS contained larger grains and showed a slightly larger bandgap than the Ga-final CIGS. We also analyzed the band alignment of the heterointerface consisting of the Zn(O,S) buffer layer/CIGS deposited by atomic layer deposition using X-ray photoelectron spectroscopy. We found that a S stoichiometric concentration of less than 20% in Zn(O,S) is essential to achieve a power conversion efficiency (PCE) of ~16.7% with conduction band offsets at 0.53 eV with 14% of S content. However, when the S content exceeded 20%, no PCE was obtained with conduction band offsets at >1 eV. Therefore, this study suggests that an appropriate S content in the Zn(O,S) buffer layer is a key factor for achieving improved PCE in Zn(O,S)/CIGS thin film solar cells

because the carrier injection at this interface is very strongly affected by the interfacial conduction band offset.

1. Introduction

Among the many types of thin film solar cells, Cu(In,Ga)Se₂ (CIGS)-based thin film solar cells are considered important. Owing to the high visible light absorption of CIGS, it is possible to achieve power conversion efficiencies (PCE) exceeding 20% in thin film solar cells using CIGS absorbers, which approaches the PCE of bulk single crystal Si solar cell.¹ The potential PCE values that can be achieved in CIGS thin film solar cells exceed the values that can be achieved with other thin film solar cells.² The typical CIGS-based thin film solar cell consists of multilayered stacks of the bottom electrode, p-type CIGS absorber, n-type buffer layer, n-type intrinsic ZnO, Al-doped ZnO, and top electrode.³ Due to the stacked structure, it is crucial to optimize the electronic structure of the interface and surface of each layer. This is known as the proposed mechanism that charge recombination is highly possible at each interface, which acts as one of the major causes for low PCE values.⁴ The band electronic structure of the CIGS-buffer layer interface is considered as an important factor, which determines the PCE and thus, a systematic spectroscopic analysis towards the construction of the band alignment of the interfaces based on measurements on the conduction band offset (CBO) and valence band offset (VBO) can provide important guidelines to improve the PCE of CIGS-based solar cells.^{5 6 7} Changing the oft-used CdS buffer layers and the use of Cd-free buffer layers is being actively explored due to environmental toxicity of Cd, and Zn(O,S) is considered as one of the main alternative buffer materials.⁸ At the interface of CIGS and Zn(O,S), the ordered vacancy compound (OVC) in the CIGS surface and the S content in the Zn(O,S) are significant factors, which control the CBO.⁵ The conductivity in the Cu-poor OVC layer is known to be controlled by the In-rich subphase acting as an acceptor or the Se-rich subphase acting as the donor.^{9 10} Hence, to achieve a CBO at 0–0.5 eV,

at which the carrier recombination is minimized and high PCE is attained, the electronic structures of both CIGS and Zn(O,S) surfaces needs to be investigated.¹¹

In this report, the PCEs of CIGS-based solar cells were correlated to the electronic structures. The solar cell with an active layer area of 0.233 cm² (the schematic structure of solar cell is shown in Fig. 1) consists of stacked layers of soda lime glass substrate, Mo electrode (sputtering), 2 μm thick Ga-final and In-final CIGS (co-evaporation process either finished by the final Ga or In-deposition), 30 nm thick Zn(O,S) (atomic layer deposition, ALD), intrinsic ZnO (RF sputtering), Al-doped ZnO electrode (DC sputtering), and MgF₂ layer for the anti-reflection coating. The Zn(O,S) buffer layers were deposited on CIGS by ALD using diethylzinc with either H₂S or H₂O gas at 115 °C. Zn(O,S) was formed by the subsequent ALD process consisting of the initial ZnO deposition and the final ZnS deposition. We investigated (1) the electronic structures of the CIGS for In-final and Ga-final processes (i.e., In- and Ga-deposition is the final stage of sequential CIGS co-evaporation) and (2) the Zn(O,S)/CIGS interfacial band alignment and CBO using various spectroscopic analyses such as X-ray photoelectron spectroscopy (XPS), ultraviolet visible (UV-vis) spectrometry, and cathode luminescence (CL). We observed a rapid change in the (1) Cu content and (2) the binding energy near the surface of the CIGS and the relative ratio of In/Ga content affects the bandgaps of CIGS, respectively. Based on the bandgaps of CIGS extracted from CL and Zn(O,S) from UV-vis measurements and XPS valence band edge analysis on the CIGS/Zn(O,S) interface, we suggest that the CBO value at the Zn(O,S)/CIGS interface as a function of the S content is a critical factor determining whether the solar cell has a high PCE (~16.7%) or a PCE of 0%.

2. Results and Discussion

2.1 Near-surface electronic structure of CIGS obtained with In-final and Ga-final deposition process

Figure 2 represents the XPS survey scan of the In-final and Ga-final CIGS surfaces before and after Ar sputtering, which etched several nm of the top surface. The stoichiometric fractions of the major elements (Cu, In, Ga, Se, O) detected in the XPS profiles calculated by atomic sensitivity factor corrections are summarized in Table I. From Table I, the stoichiometry of the In-final and Ga-final CIGS samples before Ar sputtering are $\text{CuIn}_{2.5}\text{Ga}_{5.6}\text{Se}_{2.4}$ and $\text{CuIn}_{2.8}\text{Ga}_{7.3}\text{Se}_{4.3}$, respectively. After sputtering, the surface stoichiometric compositions of In-final and Ga-final CIGS change to $\text{CuIn}_{0.7}\text{Ga}_{1.7}\text{Se}$ and $\text{CuIn}_{0.6}\text{Ga}_{1.6}\text{Se}_{0.9}$, respectively. It can be observed from Table I that the evaporation process factor in the In-final and Ga-final procedure indeed affects the In and Ga concentrations at the surface. More importantly, for all samples, the Cu/(In+Ga) ratio is significantly low (~0.1) before sputtering and the ratio increases to ~0.4 after sputtering. This Cu-poor surface region is well known as the OVC phase, which exhibits a high density of Cu vacancies. According to previous studies, the In-final CIGS sample is considered to lead to OVC with a phase composition of CuIn_3Se_5 ⁹; however, in this study, both In and Ga-final CIGS surfaces contained an OVC-like Cu-poor phase. In OVC the vacancies of Cu and Se act as acceptors and donors, respectively and therefore, greatly affect the conductivity of CIGS.¹² The high O content observed before sputtering can be ascribed to the formation of a native oxide in air, which leads to a large O concentration gradient from the uppermost surface to near-surface. This ambient O can be greatly reduced by wet etching process¹³; however, the presence of O in the top surface is unavoidable (~1 nm) from the regrowth even after the native oxide is etched and this layer can be expected to modify the electronic structure of the top surface of

CIGS. Similarly, even in the Zn(O,S)/CIGS interface of the solar cell stack, O from Zn(O,S) is also included in CIGS by diffusion-based chemical mixing.

Figure 3 shows the high-resolution Cu 2p, In 3d, Ga 3d, and Se 3d XPS profiles.

Consistent with the survey spectra in Fig. 2, it can be clearly seen that the intensity of the Cu 2p peak largely increases after sputtering, indicating the formation of surface OVC at the uppermost top surface. Also, the binding energy of the Cu 2p peak is shifted to a higher level, indicating the transition from Cu oxide in the Cu-poor top surface before sputtering to Cu in the CIGS phase at the Cu-rich near-surface after sputtering. Features of In and Se peaks did not show much difference between In-final and Ga-final samples; however, the Ga 3d peak revealed a higher intensity for Ga₂Se₃, which is a typical indicator of the Ga-final surface.¹⁴

Figure 4 represents the valence band (VB) edge spectra of the Ga-final and In-final CIGS samples. The VB edge spectra for both the samples indicate a strong p-type band structure in which the VB onset energy is markedly overlapped with the Fermi energy (E_F) level (i.e., a binding energy of 0 eV). Both the samples showed a higher VB state intensity after sputtering similar to the core binding states. It is believed that the photoelectron escape yield is significantly varied by the top O-rich surface, leading to a reduced peak intensity before Ar sputtering.

From XPS analysis, which shows marked differences in the surface chemistry of CIGS, we can expect to observe differences in the near-surface bandgap as well. **Figure 5(a)-(c)** show the scanning electron microscopy (SEM) images and CL spectra of the Ga-final and In-final CIGS. Using the SEM-CL system, the bandgap of CIGS can be analyzed at a specific local surface region. The surface roughness of the Ga-final (with fine grains) and In-final CIGS (with coarse grains) is clearly different and this suggests different surface growth mechanisms depending on the final elements. It has previously been reported that the presence of grain boundaries (GBs) in CIGS is the main origin for charge recombination at the localized surface defect.¹⁵ Consequently, In-final CIGS with coarse grains and lower

number of GBs might be preferred for low surface charge recombination. In spite that full range spectrum extending over the high energy peak shoulder was not gained due to the CL detector energy limitation, Gaussian peak fitting to the raw CL data yields the bandgaps of the Ga-final CIGS at 1.31 eV and the In-final CIGS at 1.25 eV with a deviation of ± 0.01 eV (Fig. 5c). This indicates that an increase in the In content reduces the bandgap of the CIGS. This is similar to the reduction in the bandgap observed in the case of $\text{In}_x\text{Ga}_y\text{As}_{1-x-y}$ with increase in the In content because of the relatively stronger interaction of the In 4d orbital to anions in the ionic bond configuration.¹⁶ The analysis of luminescence spectrum of CIGS using CL is a particular method to extract the bandgap but it might be slightly different from the absorption bandgap since it not only probes the near-surface region (at several μm depth) but also is involved with different energy transition processes. Therefore, the optical bandgap of In-final CIGS in UV-vis absorption spectrum was measured at 1.16 eV from the direct bandgap plot ($(\alpha h\nu)^2$ vs. photon energy, E). The energy difference of bandgap by 0.09 eV between CL data (from luminescence) and UV-vis data (from absorption) is ascribed to the different energy transition process and probing depth ranges (i.e., CL for the near surface region and UV-vis for the bulk region).

In other reports^{17 18}, the role of the thickness of CIGS in determining the PCE of the CIGS solar cell has been widely discussed. The CIGS should be sufficiently thick to show improved crystallinity and high optical absorption; however, the thickness should not be excessively large to prevent a large surface roughness-induced leakage current. In addition to the thickness of CIGS, the current study suggests that the bandgap of CIGS varies with the In-final and Ga-final evaporation process conditions and this affects the interfacial band-alignment of the CIGS buffer layer. In the light of these results, In-final CIGS was used for the solar cell fabrication in this study because it offers (1) lower GB density and (2) higher light absorption attributed to the lower optical bandgap than Ga-final CIGS.

2.2 Correlation between the CBO of the Zn(O,S) buffer-CIGS interface with different S concentrations and PCE

In order to analyze the CBO of the Zn(O,S)/CIGS interface, the bandgap of the Zn(O,S) layers deposited on soda-lime glass substrate were first determined using UV-Vis spectroscopy. **Figure 6 (a)-(c)** show the absorption coefficient spectra and their direct/indirect transition plots. In the previous studies, the bandgap bowing of Zn(O,S) as a function of S contents has been reported in spite that the actual degree of bowing varies from one to another.¹⁹⁻²¹ Thus, Zn(O,S) is not subject to the mean-field bandgap scaling as expressed by $xE_{G,ZnO}+(1-x)E_{G,ZnS}$ (i.e., x is the composition) but due to the additional effect of bowing factor, which physically originates from the complicated band-edge modifications such as the anticrossing interaction between the localized states of the substitutional minority anions and the extended states of the host conduction or valence band.²² It is also obvious that bandgap of Zn(O,S) is not only related to the O/S relative stoichiometry but also strongly affected by local bonding arrangement due to crystallinity, S site types in Zn(O,S) (i.e., either at the inside of grain or grain boundary), bonding distortion due to lattice mismatch. This structural complexity brings about dramatically different bandgaps of Zn(O,S) depending on the deposition process type and thermal treatment so that only S-content based prediction of Zn(O,S) bandgap might be subject to the physical error. Thus, a complex bandedge character of Zn(O,S) requires a careful analysis for the bandgap extraction from optical absorption data as done in other ternary II-VI compounds.^{22, 23} Here, both of direct (**Fig. 6(b)**) and indirect transition (**Fig. 6(c)**) plots were considered for the optical bandgap extraction of Zn(O,S). The linear fitting to the indirect transition plot, $(\alpha h\nu)^{1/2}$ vs. photon energy yields the absorption onset energy only slightly varying between 2.4-2.5 eV inconsistent to the reported values with a random bandgap distribution over 14-80% S contents. This result is against the previous study revealing that bandgaps in XRD-amorphous Zn(O,S) phase and S-content induced bowing effect were well analyzed with indirect transition plot.²¹ In contrast, the direct

transition plot, $(\alpha h\nu)^2$ vs. photon energy gives the regular bandgap values for low- (14%) and high (80%)-end S contents at 3.19 and 3.1 eV respectively. The S-content induced bowing effect is clearly shown although the degree of bowing is weaker than other reports.^{19, 21}

Therefore, Zn(O,S) bandgaps extracted from the direct transition plot are used for bandoffset determination.

Figure 7 shows the XPS depth profiles of the Zn(O,S)/CIGS layered samples with different S contents (14, 33, 50, and 80%) for sputtering durations ranging from 0 to 420 sec. The depth profiles of Zn 3d, In 4d, and Se 3d levels were used to define the boundaries of the Zn(O,S) bulk, Zn(O,S)/CIGS interface, and the CIGS bulk region. The concentration of each element rapidly changed along the depth; however, it is certain that samples obtained after sputtering for 0 sec and 420 sec correspond to the top Zn(O,S) surface and CIGS bulk region, respectively. The depth profiles show that all the elements (Zn, O, and S) in the buffer layer considerably diffuse into bulk of the CIGS. Zn diffusion was specifically similar for all samples, resulting in 5–10 % atomic Zn after sputtering for 420 sec. However, compared to other samples, the diffusion behavior of O and S diffusion was different only in the sample with 14% S and O diffused at higher atomic ratios, while S diffused at lower atomic ratios into the depth, in comparison to other samples with higher S content. The markedly different O and S diffusion in the sample with 14% S at the interface may be partly responsible for the CBO and PCE change since only samples with 14% S shows low CBO and effective PCE.

Figure 8 represents the VB edge spectra measured by XPS narrow scanning. The VB edge XPS spectra consist of the outermost occupied molecular orbital states so that mixed states of O 2p/S 2p/Zn 3d in Zn(O,S) and mixed metallic *nd* orbitals ($n = 3$ or 4) in CIGS are respectively the chemical origins for the VB edge states in the samples sputtered for 0 sec and 420 sec. It is found that systematic spectral change in VB edge of Zn(O,S) is found as the rise of states located at ~ 5.2 eV of binding energy as increasing S content, which should be related

to S 2p-mixed MO states. The VBO (ΔE_v) and CBO (ΔE_c) can be extracted from the optical bandgap (in Fig. 6) and the XPS VB edge binding energy by using the following equations.⁵

$$\Delta E_v = E_{V-\text{In}4d} - \Delta E_{V-\text{Zn}3d} - \Delta E_{\text{CL}} \quad (1)$$

$$\Delta E_c = E_{G-\text{Zn(O,S)}} - E_{G-\text{CIGS}} - \Delta E_v \quad (2)$$

In the above equations, ΔE_{CL} , $\Delta E_{V-\text{In}4d}$, and $\Delta E_{V-\text{Zn}3d}$ correspond to the energy difference between the In 4d and Zn3d levels, the energy difference between the VBM_{CIGS} and In 4d level, the energy difference between the $\text{VBM}_{\text{Zn(O,S)}}$ and Zn 3d level, respectively. $E_{G-\text{Zn(O,S)}}$ and $E_{G-\text{CIGS}}$ are the bandgaps of Zn(O,S) and CIGS determined by UV-vis spectroscopy and CL, respectively. The method proposed here uses a self-consistent binding energy correction, which is free of either erroneous binding energy shift or surface band-bending due to charging effect during XPS analysis. Even in Fig. 8, the VB maximum of Zn(O,S) with 14% S is determined as -0.51 eV against the E_F level (with a binding energy of 0 eV), which significantly differs from the known bulk properties of n-type Zn(O,S). This binding energy difference can possibly be attributed to the surface charging effect or band-bending because the binding energies of other elements were also subject to a similar negative shift compared to the regular value. Also, because of the rapid chemical transition from the Zn(O,S) surface, both 1st (0 sec) and 2nd (30 sec) points of XPS depth profile were considered for obtaining $\Delta E_{V-\text{Zn}3d}$.

Figure 9 (a)-(d) shows the variation of CBO and VBO values for the all samples as a function of the sputtering time. The reference position of Zn(O,S) was chosen as the Zn(O,S) surface sputtered for either 0 sec and 30 sec without any CIGS elements and then, each In 3d level at the given sputtering time was considered to calculate the VBO against these two references. As shown in Fig. 9, the slight deviation in the extracted VBO values is apparent at each depth point because the elemental fraction is also subject to a transient distribution in the depth, as shown in Fig. 7. This chemical fluctuation was treated as the average value of VBO by taking as many interfacial values as possible. In Fig. 9(a), the total number of data points

in the 20–30 nm interfacial region are about 10, indicating a 2–3 nm interval data collection, which is comparable to a minimum d-orbital coupling range in the atomic array, which is considered as a reference scale-of-order for establishing the bulk band structure.²⁴ Therefore, this level of data is considered to be sufficient to estimate the interfacial band alignment. Based on the average values of the VBO (listed in Table II), the CBO was calculated using the measured bandgap (E_G) values of Zn(O,S) and CIGS ($E_G = 1.25$ eV). As shown in Fig 9(b), the CBO for samples with S fraction of 14% is 0.53 eV, while those for all samples with high S fractions (> 20%) larger than 1 eV. This trend of CBO values is strongly correlated to the PCE values where only Zn(O,S)/CIGS with a S fraction of 14% showed a PCE of ~16.7%, while all other stacks revealed a PCE of 0%. CBO values from Fig. 9(e) clearly suggest a strong correlation between low CBO values (<~ 0.5 eV) and achieving high PCE values. It should be noted that the selection of the reference point of Zn(O,S) either at the top surface (1st point in the data) or near the surface (2nd point in the data) changes the CBO values considerably. This is due to the ambient O/OH adsorbed on the uppermost surface of the Zn(O,S) via the surface defect sites and is not related to the interfacial chemistry of the CBO determination. In this regard, we conclude that the 2nd point VBO value of the Zn(O,S) buffer layer is a better reference than the 1st one. The results of the PCE analysis of the solar cell are listed in Table III and the I-V curve shown by the solar cell is shown in **Fig. 10**. The performance of the solar cell with Zn(O,S) with a S content of 14% is comparable to that reported in a previous study, which reports a high PCE at a S content of 10–20% in the light of optimized CBO values of 0.2–0.7 eV.¹⁹ However, in another study on the ZnS buffer layer grown by chemical bath deposition with a significant ambient O inclusion (as demonstrated by XPS analysis) the CBO values at the ZnS/CIGS interface was not a factor determining the PCE.⁵ Therefore, the method by which the Zn(O,S) buffer layer is deposited is critical and it is necessary to extract the CBO based on the optical and photoelectron spectroscopic analyses with the measured data (and not from the reference data) because all the band electronic

parameters, such as bandgap and interfacial chemistry, vary largely depending on a certain process method. Compared to the CdS/CIGS-based solar cells, the fill factor (FF) and series resistance (R_s) of the Zn(O,S)/CIGS interface is somewhat higher and this suggests that further improvements in the PCE is possible by optimizing these factors as well. The solar cells having the effective PCE values of 14.6 and 13.7% were also found for Zn(O,S) buffer layers with S contents at 16 and 11% so that these also support the importance of S content less than 20%. The specific correlation between PCE and bandoffset in the narrow S contents at < 20% will be a future study.

3. Conclusions

We investigated the band electronic structure of the surfaces and interfaces of the CIGS absorber and Zn(O,S) buffer layer in correlation with the effects exerted by the S content in the Zn(O,S) on the PCE. In the case of the In-final and Ga-final co-evaporation process of CIGS, the surface chemistry analyzed by XPS before and after Ar sputtering revealed a transition from a Cu-poor and Cu oxide dominant phase to Cu-rich phase dominated by regular CIGS. The VB edge spectra indicates that all the CIGS samples show strong p-type behavior regardless of the process type but SEM-CL shows the clear differences in the surface morphology, including the grain size and bandgap between the two CIGS samples. The Ga-final CIGS showed a high bandgap (1.31 eV) and fine grains, while the In-final CIGS showed a low bandgap and coarse grains (1.25 eV). Thus, In-final CIGS was used as the solar cell absorber in this study because of its superior properties when compared to the Ga-final sample. The analysis of E_G of Zn(O,S) revealed a typical U-shaped dependence of the E_G values on the S content, which was varied from 14 to 80%. The maximum E_G extracted from the direct transition plot was 3.19 eV for a S content of 14% and the minimum E_G was 3.05 eV for a S content of 50%. The XPS depth profiling indicated that the S fraction in the Zn(O,S) buffer layer has a clear impact on the PCE and only samples with 14% S content in

the Zn(O,S) corresponding to a CBO of ~ 0.53 eV yield a PCE of 16.7%. All other solar cells with a high S fraction ($>20\%$) in the Zn(O,S) buffer yielded a PCE of 0%. In conclusion, our results suggest that optimizing the electronic band alignment of the buffer/absorber interface is a primary requirement for bringing about PCE improvement in CIGS-based solar cells with a Cd-free Zn(O,S) buffer layer.

4. Experimental

CIGS thin films, 2 μm in thickness, were deposited on soda-lime glass using a three-stage e-beam co-evaporation. Two different CIGS samples were prepared using the Ga-final and In-final co-evaporation process. The Zn(O,S) buffer layers (30 nm in thickness) were deposited on CIGS by atomic layer deposition (ALD) using diethylzinc with either H_2S or H_2O gas at 115 $^\circ\text{C}$. Zn(O,S) was formed by the subsequent ALD process consisting of the initial ZnO deposition and the final ZnS deposition. The resulting Zn(O,S) film stoichiometry was confirmed by the O/S ratio from the auger electron spectroscopy (AES) depth profile (not shown here). The ALD growth rate for Zn(O,S) was 3–4 \AA . During ALD of the buffer layer, the S concentration in the Zn(O,S) was varied from 14 to 80%. SEM-CL (Mono CL3+, Gatan) using a Ge detector was used to probe the near-surface bandgap of CIGS with a high spatial resolution (< 10 nm) at room temperature. SEM-CL excites the valence electrons to the higher level empty states by electron-beam irradiation and detects luminescence from de-excitation. The chemical composition and valence band edge states were analyzed by XPS (Thetaprobe, ThermoScientific) using Al $\text{K}\alpha$ (1486.6eV) X-ray source. In order to probe the buried interfaces of CIGS-Zn(O,S), XPS depth profiling was performed using Ar ion beam sputter etching with a differential pumped ion gun. The optical properties of Zn(O,S) and CIGS, such as the optical thickness, absorption, and optical bandgap were characterized by UV-vis spectroscopy (Cary5000 spectrometer, Agilent). In order to extract the CBO, VBO at the CIGS/Zn(O,S) interface was first measured using XPS depth profiling and then CBO was

calculated combining the VBO and the measured optical bandgap. The solar cell with an active layer area of 0.233 cm^2 consists of stacked layers of soda lime glass substrate, Mo electrode (sputtering), CIGS (co-evaporation), Zn(O,S) (ALD), intrinsic ZnO (RF sputtering), Al-doped ZnO electrode (DC sputtering), and MgF_2 layer for the anti-reflection coating. The schematic layer structure of the solar cell is depicted in Fig. 1. The I-V characteristics and the PCE of the solar cell were analyzed using the commercial solar simulator (Model WXS - 156S-10 AM 1.5, Wacom).

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