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Physicochemical Interface Effect in Cu$_2$O-ZnO Heterojunction on Photocurrent Spectrum

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Abstract

This study reports the effect of oxide heterojunction solar cell (HSC) arrangement on the solar photocurrent spectra and physical correlation to the interfacial band electronic structure. Based on $p$-Cu$_2$O/$n$-ZnO oxide junction, two types of stack arrangement were prepared to observe the solar photocurrent spectral change: FTO/Cu$_2$O/ZnO/Al and FTO/ZnO/Cu$_2$O/Al structure. As the photovoltaic cell structure, FTO was utilized for $p$-type electrode, Cu$_2$O for $p$-type semiconductor, ZnO for n-type semiconductor and Al n-type electrode. The HSC characteristics were characterized by ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy (XPS), diode current-voltage measurement, and finally, incident photon-to-current efficiency (IPCE), respectively. As a result, the IPCE spectra of HSC were large affected by (1) the band gap of first layer semiconductor which has the first light incidence regardless of the bandgap energy and (2) the interfacial electronic bandoffset values in each stack. Therefore, this result offers a possible mechanism that HSC consisting of FTO/Cu$_2$O/ZnO stack shows better IPCE response than FTO/ZnO/Cu$_2$O stack in the view of electronic band-alignment.

Keywords: heterojunction solar cell, Cu$_2$O, ZnO, IPCE, band structure

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1. Introduction

Researches on oxide heterojunction solar cell (HSC), consists of a p-n junction with different bandgap oxide layers have been actively performed because of its cost-effectiveness, facile manufacturing process control, and reliable material properties. These merits place the oxide HSC as the potential future solar cell, which can offer the technical solutions to meet current requirements in commercial solar cell industry such as low raw material price, low manufacturing cost, and easy mass-production process. Nevertheless, the power conversion efficiency (PCE) of oxide HSCs is much lower than Si and chalcogenide thin film solar cells. Although the merit of oxide HSC is related to abundancy of metal oxide species such as Cu-oxide and Zn-oxide, best PCE levels of oxide HSC have been reported only at 1-5 % unless using either rare-earth p- or n-type metal oxides. Therefore, research activities on oxide HSC are mainly focused on the improvement of PCE level.

Among many oxides considered for absorber layer, Cu$_2$O is highlighted as a p-type semiconductor with its bandgap at 2.1 eV and PCE level is theoretically expected to reach up to 17%. Since Cu$_2$O is non-toxic, naturally abundant, and can be fabricated and processed at the low cost, its various application to light emitting diode, gas sensors, and p-type absorber in solar cell is being studied.

In conventional homo-junction solar cell like Si p-n junction, the interfacial properties is well predicted and modeled so that it comes with easily controllable design factors. However, as to oxide HSCs, the interface is the most challenging part due to the significant chemical mixing of elements, non-stoichiometry, and defect/trap-site generation. In view of solar cell operation, this arises a large uncertainty about the interfacial bandoffset which determines the effective carrier separation at the junction. Although theoretical prediction was made on band-alignment model based on the previous report, the degree of precision based on such predicted models is not so high at all in the case of oxide HSC. This raises the need for experimental approaches to investigate the interfacial psychochemical properties using the proper spectroscopic techniques.

In this study, we investigated the effect of interfacial properties on photon energy dependent PCE for p-Cu$_2$O/n-ZnO HSC by changing the stack arrangement. In typical thin film HSC cell, there are the top window layer with large bandgap n-type semiconductor and then, the absorber with small bandgap p-type semiconductor at the bottom. However, we found the significant solar photocurrent spectral change in incident photon-to-current efficiency (IPCE) as reversing the stacking order to the conventional one. In order to investigate this as focusing the interfacial chemical properties and band-alignments in both p/n and metal-semiconductor junction, spectroscopic measurements using
ultraviolet-visible (UV-vis) spectrometer and X-ray photoelectron spectroscopy (XPS) measurements were carried out. This result provides a valuable guideline for Cu$_2$O-based oxide HSC structure optimization based on the electronic band-alignment.

2. Experimental

The 0.7–4 μm thick p-type cupric oxide, Cu$_2$O was fabricated on fluorine doped tin oxide (FTO) glass by electrodeposition method as applying -3 V of bias at 60°C in pH 9 solution consisting of 0.2M copper sulfate (>99.9%, Sigma Aldrich) and 3M Lactic Acid (88–92%, Sigma Aldrich) for 40 min. The 120 nm thick n-type ZnO was deposited by RF magnetron sputtering at the condition of preheating 10 min, pre-sputter 5 min, 300°C, and 1.00×10$^{-2}$ Torr under Ar 10 sccm flow. In addition, the reverse layer sequence, ZnO deposition in vacuum on FTO followed by Cu$_2$O was also applied to minimize subcutaneous oxidation of Cu$_2$O led by the high temperature ZnO sputtering. For this p-n junction, Al electrode with the thickness of 50 nm and the diameter of 100 μm was deposited by electron-beam deposition.

The diode I-V characteristic was evaluated by Keithley 2612 current-voltage (I-V) source meter. The photocurrent spectra as the function of wavelength (from 1200 to 300 nm) of monochromatic incident light generated by Xenon lamp onto Al electrode in HSC were measured to achieve IPCE results. The standard Si solar cell (BS-500, BUNKOUKEIKI Co., Japan) was utilized to calculate the IPCE. The crystal structures were analyzed by X-ray diffraction (XRD, UltimaIll, Rigaku, Japan) and the surface chemical binding state, valence band-edge state, and depth-profile were obtained by X-ray photoelectron spectroscopy (XPS, theta probe base system, Thermo Fisher Scientific Co., USA). The bandgap of each layer was determined by UV-vis spectrometer (Cary 5000, Agilent, USA) analysis.

3. Results and Discussion

The crystallinity of Cu$_2$O (at the thickness of 4.2 μm, 1.9 μm, and 720 nm) on FTO (at the thickness of 250 nm) glass as a function of thickness was evaluated by XRD from 20 to 50° of diffraction angle by the angle interval of 0.02° (Fig. 1a). XRD data revealed diffraction peaks of
Cu$_2$O corresponding to the cubic structure (JCPDS-01-071-3645, a=0.42685nm) having (110), (111), and (200) plane at 29.66°, 36.54°, and 42.33° respectively. The 1.9 μm thick sample shows the strongest XRD peaks among samples even than the thickest (4.2 μm) sample, indicating the crystallinity does not scale with the film thickness as in the film deposited by vacuum deposition. Based on the XRD peak intensity, the preferential crystal plane of Cu$_2$O is also changed from (200) for 720 nm and 1.9 μm thick films to (111) for 4.2 μm thick film. Upon fabrication of diodes, the best diode results were obtained at 720 nm thick Cu$_2$O film while diodes with other Cu$_2$O films revealed the poor performance (not shown here). This indicates that the bulk crystallinity of Cu$_2$O film is not a decisive but only partial effect to control the diode characteristic. We rather consider that interface of Cu$_2$O/ZnO is more relevant to the diode property. SEM data in Fig. 1(b) and (c) reveal the cross-sectional morphology of FTO/ZnO/Cu$_2$O and FTO/Cu$_2$O/ZnO stack respectively. In order to distinguish each layer easily, the target thickness of each layer was set to 200 nm for ZnO and 500 nm for Cu$_2$O but the interface formation leads to variation in the resulted thickness from SEM images. Each layer was formed as a continuous film and energy dispersive spectroscopy analysis on the specific spots identified the distinctive Cu and Zn in CuO and ZnO layer respectively as shown in atomic % plots of Fig 1(b) and (c).

UV-vis spectroscopy analysis was performed to achieve the optical bandgap to be used for the electronic band structure model by taking absorbance and transmission data (Fig. 2). In Fig. 2 (a) and (b), Cu$_2$O has the high absorbance at 300-500 nm of wavelength, corresponding to UV and all visible range and this confirms that Cu$_2$O has a clear advantage to absorb the incident light and produce photo-carriers in the visible range. In Fig. 2 (c) and (d), ZnO revealed the strong absorbance at < 400 nm of wavelength and its high transparency at > 80% in the visible range, which makes ZnO the ideal material for the window layer of solar cell. The optical bandgap from UV-vis absorbance data was extracted by Tauc plot in Fig. 3. Tauc plots ((αhν)^n vs. hν) curves were plotted for different n (n= 1/2, in the case of direct band gap) values, α is the absorption coefficient calculated from absorption spectra and photon energy. The direct bandgaps of Cu$_2$O and ZnO were 1.4 and 3.2 eV respectively. However, the typical Cu$_2$O optical bandgap is ~ 2.1 eV and this bandgap difference is related to the formation of CuO at the electrodeposited Cu$_2$O surface, which rapidly occurs in air ambient. Indeed, the absorbance data in Fig. 2(a) shows the marked absorbance in the wavelength down to 1100 nm, which is due to light absorption in the surface CuO subphase. The effect of stack arrangement of Cu$_2$O and ZnO layers on the optical property was investigated by UV/vis
analysis in Fig. 4. The stack of FTO/Cu₂O/ZnO/Al shows the lower absorbance in the range of 600-1000 nm than the reverse stack arrangement (FTO/ZnO/Cu₂O/Al) but with no difference in the range of 300-500 nm, which is the high absorbance band. Therefore, it is deduce from Fig. 4 that the stacking arrangement has an outstanding impact on degree of CuO phase formation on Cu₂O surface, leading to absorbance at 500-1100 nm but no effect on the strong absorption region due to ZnO and Cu₂O phase.

I-V results in Fig. 5 shows the p/n diode characteristics of differently stacked oxide junctions. Both junctions revealed the regular diode property with the asymmetric I-V behavior with bias polarity. However, the bias polarity with forward current is different depending on the junction type; – bias for ZnO/Cu₂O (n/p) junction (Fig. 5(a)) and + bias for Cu₂O/ZnO (p/n) junction (Fig. 5(b)). It is noted that the diode rectification of ZnO/Cu₂O is inferior to Cu₂O/ZnO since CuO subphase formed on Cu₂O generates the additional energy barriers for charge transport. Under the dark-current condition, the rectification factor of each diode at ± 5V is 2 for ZnO/Cu₂O and 30 for Cu₂O/ZnO stacks. The photo-current is clearly observed in both diodes upon the light exposure condition and particularly, the ratio of photo-current/dark-current for Cu₂O/ZnO is > ~10³, offering a good visible photo-response performance. The repeated I-V curves with 10 cyclic sweeps and time-dependent transient photo-current traces under the continuous bias at 2V are shown in Fig. 5(c) and (d) for each stack. It turns out that Cu₂O/ZnO stack has an outstanding dark-current baseline drift compared to ZnO/Cu₂O without (1) a noticeable change in the net photo-current level and (2) no residual lag in time-dependent photo-current transition. This suggests that FTO/Cu₂O/ZnO stack has a high number of non-photoactive charge trap sites, which is considered to be intrinsically formed at FTO/Cu₂O interface, which is the different interface from FTO/ZnO interface in FTO/ZnO/Cu₂O stack.

Figure 6 shows IPCE spectra to investigate the spectral response of photocurrent as changing stack arrangement. In IPCE spectra for Cu₂O/ZnO junction, three distinctive photo-current bands are observed at <400, 400-600, and 900-1200 nm of wavelength. Based on optical absorption data in Fig. 4, each band corresponds to the photo-carrier generation in ZnO (< 400 nm) and Cu₂O (400-600, 900-1200 nm). However, ZnO/Cu₂O junction shows the overall low IPCE spectra except the wavelength range at 1000-1200 nm in spite that the optical absorption in ZnO/Cu₂O is almost same as Cu₂O/ZnO and its optical absorption in the long wavelength range at 1000-1200 nm is even higher than Cu₂O/ZnO junction. The relatively high IPCE at 1000-1200 nm in ZnO/Cu₂O junction is
regarded due to CuO subphase, the bandgap of which is 1036 nm or 1.2 eV.\textsuperscript{15,21,22} The lower IPCE in ZnO/Cu\textsubscript{2}O junction compared to Cu\textsubscript{2}O/ZnO junction over the most wavelength range indicates that the electronic band alignment affected by CuO subphase on Cu\textsubscript{2}O plays a crucial role in IPCE. Therefore, XPS analysis was performed to evaluate the band alignment structure of each junction. PCEs of Cu\textsubscript{2}O/ZnO HSC are reported to be 0.1 to 3 %.\textsuperscript{2,3,14,23} The PCE level of Cu\textsubscript{2}O/ZnO HSC in this study is ~ 0.1%, requiring more optimization. Nevertheless, IPCE reaching 25% between 800-1200 nm of wavelength is not reported in other works\textsuperscript{1,3,24} so that can be considered to compensate a low PCE level in the long wavelength range.

Fig. 7 (a) and (b) represents XPS depth profiles (atomic elemental percent as a function of Ar sputtering time) for (1) FTO/Cu\textsubscript{2}O and (2) Cu\textsubscript{2}O/ZnO respectively. For sample (1), the FTO-Cu\textsubscript{2}O interfacial band alignment and CuO band structures are determined and for sample (2), the Cu\textsubscript{2}O/ZnO interfacial band alignment is obtained. The Ar sputtering condition was 0.2 nm/sec (referenced to SiO\textsubscript{2}) and the sputtering raster area was 1 mm\textsuperscript{2}. In Fig. 7(a) for FTO/Cu\textsubscript{2}O, the position at 0 sec of sputter time (or etch time) corresponds to Cu\textsubscript{2}O top surface and 150 sec of sputter time is considered as FTO with a reduction of Cu-2p atomic percent. In Fig. 7(b) for Cu\textsubscript{2}O/ZnO, the position at 0 sec of sputter time corresponds to ZnO top surface with high atomic percent of Zn-2p, at 300-400 sec is the interfacial region, and at >500 is considered as Cu\textsubscript{2}O with the rapid increase of Cu-2p atomic percent. From the XPS depth profile, the elemental information along the depth position is identified, Cu-2p binding states were analyzed at the specific points at the surface and bulk for each sample. As shown in Fig. 7(c), at the Cu\textsubscript{2}O top surface in sample 1 (0 sec of sputter time), CuO (933.4 eV) and Cu(OH)\textsubscript{2} (934.7 eV) binding states are resolved and satellite peaks of CuO (Cu(2+)) appear at 943.8 and 941.3 eV. This bond character clearly indicates that Cu\textsubscript{2}O surface in sample 1 has CuO subphase. In the bulk region of sample 1 (150 sec of sputter time), only Cu\textsubscript{2}O binding state (932.6 eV) is resolved without CuO subphase features (Fig. 7c). On the other hand, sample 2 revealed only Cu\textsubscript{2}O binding state (932.6 eV) in both surface and bulk region without any CuO-associated binding states and satellite peaks (Fig. 7d). This confirms the formation of subcutaneous CuO-free Cu\textsubscript{2}O/ZnO interface in sample 2 due to the deposition of ZnO in vacuum onto CuO in the sputtering chamber without air exposure.

At the specific point of sample, valence band maximum (VBM) as referenced to the Fermi energy level (E\textsubscript{F}) level was extracted by inspecting onset energy of the valence band edge XPS spectra. VBMs at the ZnO bulk (30 sec of sputter time in Fig. 7(b)) and at the Cu\textsubscript{2}O bulk (1170 sec of sputter
time) are 1.75 eV (Fig. 8(a)) and 0.18 eV (Fig. 8(b)) respectively. Using similar experimental approach combined with optical bandgap data in Fig. 3 and reference data for metal work functions and electron affinities, band alignments containing conduction band offset (CBO) and valence band offset (VBO) as referenced to $E_F$ level are calculated for FTO/ZnO, FTO/Cu$_2$O, CuO/Al, and ZnO/Al interfaces to construct the band alignment model in Fig. 8 (c) and (d) for FTO/Cu$_2$O/ZnO/Al (i.e., stack 1) and FTO/ZnO/Cu$_2$O/Al (i.e., stack 2) arrangements respectively. First, when the semiconductor work function is larger than metal electrodes at the interface of electrodes and the semiconductor junction such as FTO/ZnO and Al/Cu$_2$O, calculation of the barrier height ($V_o$) of the Schottky diode is done using Eq. (1).

$$\phi_s - \phi_m = V_o \quad (\phi_m < \phi_s)$$

(1)

Where $\phi_s$ is the work function of semiconductor and $\phi_m$ is the work function of metal.

Also, from the theory introduced by Kraut, the VBO ($\Delta E_v$) can be calculated by Eq. (2) and (3) as following:

$$\Delta E_v = E_{VB}^B - E_{VB}^A + \left[ \left( E_{CL}^A - E_{CL}^{A/B} \right) + \left( E_{CL}^{B/A} - E_{CL}^B \right) \right]$$

(2)

$$\Delta E_c = E_g^B - E_g^A + \Delta E_v$$

(3)

Where $E_{VB}^B$ and $E_{VB}^A$ are bulk A and B materials core-level energies and $E_{CL}^{A/B}$ and $E_{CL}^{B/A}$ are the same core-level energies of A and B at the interface. The CBO ($\Delta E_c$) can then be calculated using the Eq. (2) and (3). In our experiment setup, since the light incidence occurred onto Al electrode, CuO subphase present at the surface of Cu$_2$O in stack 2 first absorbs the high portion of light due to its low bandgap. The major optical absorption of CuO subphase is present in stack 2 so that the effective photo-carrier generation in Cu$_2$O, inserted as absorber, is substantially reduced. In addition, the hole transport in stack 2 is rather reduced in the both direction of Cu$_2$O→CuO (VBO at 0.22eV) and Cu$_2$O→ZnO (VBO at 1.49 eV) as limiting hole photo-current (Fig. 8(d)). In stack 2, the direction of electron transport can occur both directions: (1) from Cu$_2$O to FTO and (2) CuO to Al so that it may lead to the electron-hole recombination in CuO. On the other hand, in stack 1 (Fig. 8(c)), the incident light is mostly absorbed by Cu$_2$O without perturbation of CuO subphase since ZnO has the large UV-range bandgap at 3.2 eV. Furthermore, electron transport from Cu$_2$O to Al via ZnO is drifted by the downward band alignment without CBO and hole transport from Cu$_2$O to FTO is also
facile with VBO at 0.26 eV. As a consequence, the band-alignment model explains electronic band features about the light absorption for photo-carrier generation, separation, and transport with experimentally defined CBO and VBO values in each HSC arrangement. 1

4. Conclusions

This article reports the spectral change in solar photocurrent upon altering arrangement of Cu$_2$O and ZnO layer in oxide HSC. Based on XPS analysis, top surface Cu$_2$O has subcutaneous CuO subphase layer upon air ambient exposure in the case of FTO/ZnO/Cu$_2$O arrangement, which diminishes the light absorption in Cu$_2$O because of the high light absorption in the small bandgap (1.4 eV) subcutaneous CuO surface layer. As a result, FTO/ZnO/Cu$_2$O/Al HSC stack has much lower IPCE over the entire wavelength than FTO/Cu$_2$O/ZnO/Al stack. The band-alignment analysis, combining VB-edge XPS spectra (for VBM), UV-vis data (for optical bandgap), and reported work function and electron affinity values, yields the full electronic band-structure and alignment for each stack. From this, the first layer receiving incident light is most important for solar photocurrent spectra since it decisively affects IPCE by altering the dominant light absorption features in the stack and VBO and CBO in band electronic structure for charge transport. The CuO subphase in ZnO/Cu$_2$O stack is negative for all these respects but CuO/ZnO stack has the clear advantage in band-alignment with no CBO and very small VBO values. This study therefore highlights the importance of band-alignment characterization to clarify the photo-current mechanism in oxide HSC based on experimental analysis for efficiency optimization.

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6. References

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Figures and Captions

Figure 1. (a) XRD patterns of Cu₂O with different thickness (red: 720 nm, black: 1.9 μm, blue: 4.2 μm) and SEM (left) and atomic fraction (right) extracted from EDS spot analysis at each layer (spectrum
1-3) of (b) FTO/ZnO/Cu$_2$O and (c) FTO/Cu$_2$O/ZnO stacks. In XRD pattern, reference diffraction peaks from JCPDS card are shown together.

Figure 2. UV-vis absorbance and transmittance spectra: (a) absorbance and (b) transmittance of Cu$_2$O, (c) absorbance and (d) transmittance of ZnO.
Figure 3. The extracted optical band gap of (a) Cu$_2$O and (b) ZnO from Tauc plot.

Figure 4. (a) Absorbance and (b) transmittance spectra of the whole stacks of FTO/ZnO/Cu$_2$O/Al and FTO/Cu$_2$O/ZnO/Al.
Figure 5. I-V characteristics of (a) FTO/ZnO/Cu$_2$O/Al and (b) FTO/Cu$_2$O/ZnO/Al under light-off (dark-current) and light-on (photo-current) condition. The repeated I-V (left) and I-t curves (right) of (c) FTO/ZnO/Cu$_2$O/Al and (d) FTO/Cu$_2$O/ZnO/Al.
Figure 6. IPCE spectra of (red) FTO/ZnO/Cu$_2$O/Al and (black) FTO/Cu$_2$O/ZnO/Al.
Figure 7. XPS depth profile of (a) FTO/Cu$_2$O atomic %, (b) ZnO/Cu$_2$O atomic % and Cu-2p narrow scan in the surface and bulk in (c) FTO/Cu$_2$O (etch time at 0 sec for surface and 150 sec for bulk) and (d) ZnO/Cu$_2$O (etch time at 210 sec for surface and 600 sec for bulk).
Figure 8. Valence band-edge XPS spectra with VBM values for (a) ZnO (at 30 sec of etch time) for and (b) Cu$_2$O (at 1170 sec of etch time) in FTO/Cu$_2$O/ZnO stack. The electronic band structure and alignment of (c) FTO/Cu$_2$O/ZnO/Al and (d) FTO/ZnO/Cu$_2$O/Al stacks. In FTO/Cu$_2$O/ZnO stack, there is no marked CBO and VBO to inhibit the charge separation at each interface. However, in FTO/ZnO/Cu$_2$O stack, hole transport toward FTO is blocked by the large VBO at ZnO/Cu$_2$O and CuO subphase present at Cu$_2$O surface leads to significantly different electronic band alignment from that in FTO/ZnO/Cu$_2$O.