The Electronic States of Copper Oxides Photoactive Layers Prepared by Electrodeposition followed by Annealing

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Abstract. The copper oxides are best performing metal oxide materials regarding solar energy conversion, and due to their abundance, scalability, ease of fabrication and subsequently being low-cost, Cu₂O and CuO have attracted extensive attraction. In this research, Cu₂O layers were electrodeposited on Ga:ZnO (GZO) and annealed to form directly-stacked GZO/Cu₂O/CuO. The external quantum efficiency (EQE) of the devices was evaluated which demonstrated peculiar negative regions around 500 nm besides the typical 410 nm originating from the Cu₂O. Reversed bias voltages were applied to investigate the changes, and along with the disappearance of negative regions, a peak around 550 nm and an absorption edge at 850 nm appeared, which increased with the increment of bias voltage. To elucidate the mechanism, the electronic states were investigated by x-ray photoelectron spectra (XPS). Species identification was also successful which showed the presence of CuO on the topmost layer and the underlying Cu₂O, which was difficult to analyze by XRD due to its thinness. The schematics of the band-alignments were drawn based on the calculations from the XPS measurements. The conduction band of the Cu₂O appeared elevated, which contributed to the speculated two-way flow of the charge when illuminated, and explains the appearance of the negative EQE regions. The charge transportation was successfully controlled and aligned when bias voltages were applied, which caused the disappearance of negative regions and the appearance of the absorption edge of the CuO.

1. Introduction
One ultimate goal of researches in the solar energy conversion field is to reach grid parity for worldwide deployment to reduce greenhouse gas emissions and cut down dependence on fossil fuels. As such, the cost of the material and fabrication of photovoltaics or photocathodes should be minimized, and a shift of focus to earth-abundant photovoltaic materials is imperative in realizing sustainability. Being environmental-friendly (nontoxic) is also a huge advantage. Photovoltaic materials satisfying all mentioned demands are the copper oxides, which are unique among oxides being intrinsically p-type, and also are among the best performing metal oxide materials. The copper (I) oxide (Cu₂O) and copper (II) oxide (CuO) possess bandgap energies of 2 eV and 1.5 eV respectively, with Cu₂O possessing a theoretical hydrogen conversion efficiency of 18% in water splitting and a theoretical power conversion efficiency of 20% as a solar cell. CuO possesses lower bandgap energy, absorbing corresponding light wavelengths below ~850 nm. As one single light-absorbing material cannot satisfy the wide span of the sunlight spectrum, a strategy to combine Cu₂O and CuO to utilize multiple bandgaps was reported,[1] which showed that both oxides could simultaneously act as the light-absorbing layer.
Our previous research has demonstrated the fabrication of Cu$_2$O/CuO layer by annealing in air, and also the external quantum efficiency (EQE) behavior of the directly stacked GZO/Cu$_2$O/CuO under reversed bias voltage which resembles the working condition during water splitting.[2] However, the species identification was insufficient due to the thinness of the CuO film which made the characterization of X-ray diffraction difficult. The need for detailed X-ray photoelectron spectroscopy (XPS) for the directly stacked Cu$_2$O/CuO arose not only to more accurately determine the chemical state and identification of fabricated copper oxide but also to investigate their energy states. Negative regions of EQE were observed in some of the devices when reversed bias voltage was not applied, which indicated the presence of two distinct charge transportations which might originate from two separate electric fields, presumably at the heterointerfaces of GZO/Cu$_2$O and Cu$_2$O/CuO, and XPS characterization could give insight regarding the carrier transport mechanism.

2. Experimental

2.1. Device Preparation: Electrodeposition and Annealing

Conductive gallium-doped zinc oxide (GZO)-coated glass was partly used as substrates due to its ability to demonstrate the EQE behavior of Cu$_2$O without any intermediary layer. Electrodepositions of Cu$_2$O layers were carried out from alkaline aqueous solution (pH 12.5) containing 0.4 mol L$^{-1}$ copper (II) acetate monohydrate (Cu(CH$_3$COO)$_2$·H$_2$O, Nacalai Tesque, Inc.) and 3 mol L$^{-1}$ lactic acid (Kanto Chemical, Co., Inc.). A standard 3-electrode cell was used for the potentiostatic electrodeposition with a Pt plate as the counter electrode and Ag/AgCl in saturated KCl as the reference electrode. The electrodepositions were carried out with a potentiostat (Hokuto Denko, HAL-3001) and a Coulomb meter (Hokuto Denko, HF-301) with the potential and electrical charge set at -0.4 V and 1.5 C cm$^{-2}$ respectively, and the water bath temperature set at 313 K. ZnO electrodepositions on FTO were deposited with the similar method from a solution of 80 mmol L$^{-1}$ zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, Nacalai Tesque, Inc.) in a water bath of temperature 336 K.[3]

Annealing of the devices was carried out on an alumina plate in a quartz holder, annealed at various temperatures of 523, 573 and 673 K in a rapid thermal annealing furnace (MILA 5000) for GZO-based devices. The annealing rate was set at 10 K s$^{-1}$ and the heating time was set at 60 min after the target temperature had been reached.

2.2. Characterizations

X-ray photoelectron spectroscopy (XPS) measurements were performed with a scanning X-ray microprobe (Quantera SXM-CI) made by ULVAC-PHI Inc, with a 24.8 W monochrome Al K$_\alpha$ (1486.6 eV) with a 100-μm-beam. To lessen the drift caused by charge-up, the neutralizer was operated at 1.0 V of 20 μA, and peak corrections of C 1s were made to 284.8 eV. The software used for the analyses was CasaXPS (Casa Software Ltd.)

The external quantum efficiency (EQE) measurements were performed using a monochromator (Bunko Keiki, SM-250 KB) with approximate monochromatic light intensity above 5 mW cm$^{-2}$. Reversed bias voltages were applied to investigate the carrier transportation and also simulate approximate conditions when the photoactive layers were to be used as photocathodes for water splitting.

3. Results and Discussions

3.1. The Behavior of External Quantum Efficiency (EQE) of Cu$_2$O/CuO

Figure 1 (a) shows the EQE of the 523K-annealed device without and under bias voltage of −0.01 to −0.1 V, with −0.01 V increments. Observed is the appearance of a new absorption edge around 850 nm with the increase of voltage. Without any biased voltage applied (0 V), the 523-K-prepared directly-stacked photoactive layer showed a peak at approximately 410 nm and a dip in the spectra towards the negative region around 500 nm, indicating two distinct charge transportations from different light-absorbing layers. The peak at 410 nm can be attributed to the characteristic EQE peak of electrodeposited Cu$_2$O as already reported.[4] The overall low performance may be attributed to the
formation of scattering defects such as pores during the oxidation of the Cu₂O, which involves the transportation of Cu ions.[1,4,5]

Before annealing, all charge collected can be attributed to the flow from photo-induced (starting from 650 nm) electrons from the Cu₂O layer towards the direction of the source of irradiation and extracted via the GZO layer. [4] For the 523-K-device, the dip towards the negative region in the EQE spectra within 470 and 580 nm then reveals the presence of photo-induced electrons moving in the opposite direction. Increment of reverse biased voltages by −0.001 V towards −0.01 V caused a dramatic increase in the 550-nm-peak, while the increase in the peak at around 410 nm was gradual in comparison. This also indicates that the charge collection as represented by these peaks were constituted by charges originating from more than one light-absorbing layer, which were the Cu₂O and CuO layer. Also, a distinct absorption edge for the peak of 550 nm at around 850 nm emerged. This absorption edge can be attributed to the characteristic absorption edge of CuO, as can clearly be seen from the absorption spectra of the 673 K device as already reported, which among the devices, possesses the thickest layer of CuO at the surface.[2] This behavior of dipping of the EQE curve towards the negative region was not observed when annealed in vacuum at the same temperature, even though the Cu₂O was prepared similarly, as previously reported.[4] This means that the EQE behavior is specific to devices annealed in a normal atmosphere which can be attributed by the appearance of Cu₂O/CuO internally-stacked layer. Also shown are the EQE spectra of 523, 573 and 673 K annealed devices as already reported.[2]

Figure 1. EQE spectra of (a) 523-K annealed device without and under reversed bias voltage, (b) 523, 573 and 673-K annealed devices.

3.2. Surface X-ray Photoelectron Spectroscopy (XPS)

Figure 2 shows the Cu 2p₃/₂ and CuL₃M₄,5M₄,5 spectra of the as-deposited and annealed devices. One significant change observed for the Cu 2p₃/₂ spectra is the overall shifts of the main 2p₃/₂ peak from 932.3 eV (as-deposited) to 933.1 eV (523 K), 933.4 eV (573 K), and 993.5 eV (673 K), which also showed broaden peaks. These values seem to increase from reported literature average values of the binding
energies of 932.4 eV belonging to Cu$_2$O, to 933.6 eV of CuO, based on the NIST Database,[6] as compiled by Biesinger, who reported an extensive analysis of copper XPS.[7] Another significant change observable from the Cu 2p$_{3/2}$ spectra is the emergence of satellite peaks at approximately 941.5 eV and 944 eV for the annealed devices. These evident peaks are characteristic shake-up satellites which indicate the presence of Cu(II) species, originating from the surface CuO layer.[8–13] The CuL$_3$M$_{4,5}$M$_{4,5}$ spectra as shown in figure 2 (b) indicates a shift in peak position from 916.7 eV to 917.6 eV. The peak value of the as-deposited device at 916.7 eV was close to the reported value of 916.5 eV belonging to Cu$_2$O.[14] While the Auger main peaks of Cu(I) and Cu(II) species are close to each other, the CuL$_3$M$_{4,5}$M$_{4,5}$ spectral line-shape can provide information about species differentiation.[15] The shoulder peaks at around 912-914 eV are usually observed for the spectra of CuO. In short, the spectra of the annealed devices showed XPS characteristics leaning to Cu$_2$O for the as-deposited device and CuO for the annealed layers.

![Figure 2](image-url)

**Figure 2.** The surface (a) Cu 2p$_{3/2}$ and (b) CuL$_3$M$_{4,5}$M$_{4,5}$ spectra with horizontal axes as binding and kinetic energy respectively, for the as-deposited GZO/Cu$_2$O device, and devices annealed at 523, 573, and 673 K. Along with peak shifts, the appearance of characteristic shake-up satellites in (a) and changes in spectral line-shapes in (b) can be observed here, as denoted with arrows.

Wagner has shown the chemical shifts for Auger transitions involving electrons in the atomic core and changing of the line shape for Auger transition involving valence electrons and introduced the concept of Auger parameter based on the idea that two line energies (Auger and photoelectron) of the same element in the same measurement is fixed, and the charge corrections to individual peak measurements can be canceled off and the work function corrections are not necessary.[16–18] The Auger parameter \( \alpha' \) is defined as,[19]

\[
\alpha' = \alpha + h\nu = E_b(C' C'' C''') + E_b(C)
\]

where \( E_b(C' C'' C''') \) is the kinetic energy of the Auger transition involving electrons from the \( C', C'', \) and \( C''' \) core levels, and \( E_b(C) \) is the binding energy of the photoelectron from core level \( C \). In other words, the sum of Cu 2p$_{3/2}$ peak value in binding energy and the CuL$_3$M$_{4,5}$M$_{4,5}$ peak value in kinetic energy gives the value of a characteristic modified Auger parameter which could be used to identify species. This method was effectively used by Goh et al. in assigning Cu$_2$S and CuS,[14] besides Poulston et al. who have used CuLM and the Auger parameter to distinguish Cu(0), Cu(I) and Cu(II).[8]. Calculated values are summarized in Table 1 below.

| Temperature | As-depo. | 523 K | 573 K | 673 K |
|-------------|----------|-------|-------|-------|
| Binding Energy | 932.33 | 932.42 | 932.07 | 932.33 |
| Kinetic Energy | 916.74 | 917.31 | 917.53 | 917.62 |

*Table 1. Auger Parameter calculation of as-deposited, 523 K, 573 K, and 673 K devices.*
|                  | Binding Energy | Kinetic Energy | Auger Parameter |
|------------------|----------------|----------------|-----------------|
|                  | Cu 2p 3/2      | CuL3M4,5M4,5   |                 |
| As-deposited     | 932.33         | 916.74         | 1849.07         |
| 523 K            | 933.07         | 917.31         | 1850.38         |
| 573 K            | 933.42         | 917.53         | 1850.95         |
| 673 K            | 933.57         | 917.62         | 1851.19         |

The literature average compiled values from the NIST database[6] are 1849.2 for Cu$_2$O and 1851.5 for CuO[7,20], which are near to the calculated Auger Parameter values of 1849.1 for as-deposited and 1851.2 for 673 K. Both 523 K and 573 K devices possess Auger Parameter approaching the value for CuO. Thus, it is safe to assume that the topmost layers of all annealed devices consist of CuO layers, consistent with the FESEM observations as previously reported.

3.3. Band-alignment Calculation of Cu$_2$O/CuO

The difference in valence band maximums (VBM) of the Cu$_2$O and CuO which is the valence band offset (VBO, denoted as $\Delta E_V$), is needed to understand the band-alignment of the heterojunction which was formed after annealing. By using the core-level alignment, a more accurate band offset calculation that does not rely on shift correction could be done as shown in the following equation,[21,22]

$$\Delta E_V = \left( E_{\text{CuO}}^{2p} - E_{\text{CuO}}^{2p} \right) \left( E_{\text{Cu}^{2+}}^{2p} - E_{\text{VBM}}^{2p} \right) - \left( E_{\text{Cu}^{2+}}^{2p} - E_{\text{VBM}}^{2p} \right) \quad (2)$$

where $E_{\text{CuO}}^{2p}$ is the 2p main peak value of the surface CuO, $E_{\text{Cu}^{2+}}^{2p}$ is the 2p main peak value of the underlying Cu$_2$O, $E_{\text{Cu}^{2+}}^{2p}$ is the Cu 2p main peak value of the underlying Cu$_2$O, $E_{\text{VBM}}^{2p}$ is the measured valence band maximum (VBM) of the underlying Cu$_2$O, and $E_{\text{VBM}}^{2p}$ is the measured VBM of the surface CuO. After the initial surface CuO measurement, to expose the underlying Cu$_2$O, sputtering was carried out for 18 seconds from the top surface until 180 seconds and the XPS spectra recorded for each annealed device.

The Cu 2p binding energies for the main peaks of the surface CuO ($E_{\text{CuO}}^{2p}$) were 933.1, 933.5, and 933.7 eV, which were close to the reported value of 933.6 eV.[7] It was found that sputtering during the first 18 seconds had sufficiently removed the topmost CuO layer for all annealed devices, and the average Cu 2p binding energies for the main peaks of the underlying Cu$_2$O ($E_{\text{Cu}^{2+}}^{2p}$) were 932.6, 932.4, and 932.6 eV for 523, 573, and 673 K respectively, which were close to the reported value of 932.4 eV. Also, the $E_{\text{VBM}}^{2p}$ and $E_{\text{VBM}}^{2p}$ values were extracted from the XPS spectra in the vicinity of 0 eV binding energy, along with all summarized values needed for the VBO calculations, are shown in figure 3. The above VBO calculation is the typical method calculating p-n junction band alignment, where all the peaks may appear on a single spectrum. However, for our measurement, the first sputtering had completely exposed the underlying layer, and by assuming that the spectra do not shift during continuous measurement after sputtering, the VBM could be easily calculated by calculating the difference between measured $E_{\text{VBM}}^{2p}$ and $E_{\text{VBM}}^{2p}$.
Figure 3. The XPS spectra showing all measurements needed to determine the VBO for the 523, 573 and 673 K annealed devices. The as-deposited values are for reference.

Figure 4 shows the Tauc plots for the as-deposited device and for the 673 K-annealed devices which showed a clear absorption edge for the CuO layer at 850 nm. These bandgap energies for the band offset calculations were estimated from previously measured absorbance spectra.[2] The relationship between optical bandgap energy, $E_g$ and the absorption coefficient $\alpha$ calculated from the absorbance and thickness can be represented by equation 3 as follows[23]:

$$\alpha h \nu = A(h \nu - E_g)^{n/2}$$

Equation 3

where $A$ is a constant, $h \nu$ is photon energy, for thin films $n=1$ for direct transition, and $n=4$ for an indirect allowed transition. For the as-deposited device, the direct bandgap estimated was 2.05 eV, corresponding to reported values of 2.1 eV belonging to Cu$_2$O.[24] For the 673 K-annealed devices, the direct bandgap estimated from this figure was 1.56 eV, while the indirect bandgap was 1.47 eV which were close to the reported CuO direct bandgap values by Nakaoka et al. of 1.56 eV and 1.45 eV which were heat-treated at 573 and 773 K respectively.[23] However, the actual type of bandgap energy of CuO remains controversial.[25–30]

Using the direct bandgap for Cu$_2$O as 2.05 eV and indirect bandgap for CuO as 1.47 eV from the Tauc plots, the calculated VBO values were then 0.22, 0.38, and 0.38 eV for the 523, 573 and 673 K annealed devices.
devices, respectively. The conduction band offsets (CBO) calculated were 0.8, 0.96 and 0.96 eV. The schematic band alignments are shown in figure 5.

**Figure 5.** The schematic band alignment of Cu$_2$O/CuO based on calculated VBO and bandgap energy estimated from Tauc Plots. (a) is 523 K, (b) is 573 K, and (c) 673 K.

The CBO of the 573 and 673 K-annealed devices were higher than the 523 K-annealed device, contributing to dimmed EQE performances due to higher recombination rates. In an attempt to further comprehend the charge collection mechanism of GZO/Cu$_2$O/CuO which is closely related to the appearance of EQE spectra, reference is made to the following figure 6, which shows the band alignments at equilibrium and under reversed bias voltage.

**Figure 6.** The schematic band alignment of GZO/Cu$_2$O/CuO speculated at (a) equilibrium and (b) under reversed bias voltage.

At equilibrium (0 V), the conduction band of the Cu$_2$O should appear elevated against both the GZO and CuO layers. Here, charges originating from the Cu$_2$O nearby the GZO/Cu$_2$O heterojunction flowed towards the GZO layer and appeared as the EQE peak at around 410 nm. However, the charge originating from the CuO, or deep in the Cu$_2$O layer near the vicinity of Cu$_2$O/CuO can favorably flow in the opposite direction towards the Au electrodes, which explains the negative regions in the EQE around 500 nm. When reversed bias voltage was applied, the potentials across the heterojunctions were
increased, as denoted with $eV_r$, which exaggerated depiction is shown in figure 6(b). Consequently, along with the formation of quasi-Fermi levels, the band energy at the CuO side was relatively raised, facilitating movements of photo-induced electrons in the CuO layer towards the Cu$_2$O layer when irradiated. This should enable more charge collection via the GZO layer, which mechanism corresponds to the EQE measurement. The depletion width and the peak electric field at the junctions were also increased in this condition,[31] which explains the heightened peak at 410 nm. On the other hand, the higher rate of increase in peak 550 nm along with the reversed bias voltage suggests not only that charges originating from the Cu$_2$O which once flowed in two directions were corrected and aligned, but also the contribution of charge originating from the CuO layer, which is also evidenced by the appearance of absorption edge at 850 nm.

4. Conclusions
The EQE of the directly-stacked Cu$_2$O/CuO photovoltaic layers and their changes under reversed bias voltage was shown, giving insights into the change in charge transportation. The EQE demonstrated the ability of both Cu$_2$O and CuO layers to act as light-absorbing layers, which showed an augmented light-absorption span. The band-alignments were calculated and the mechanism of the EQE behavior was elucidated by investigation of the energy states. The results show that Cu$_2$O/CuO may work well as photocathodes in water splitting under applied biased voltage, and better optimization could be carried out to further improve the Cu$_2$O/CuO as a photovoltaic device to utilize its ability for a superior light-absorption span. This research also highlights the importance of minimal defects for a better semiconductor quality and may provide insights for an improved band-alignment for future fabrication of the Cu$_2$O/CuO photoactive layer.

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