# STRUCTURAL AND ELECTRONIC PROPERTIES OF ELECTRODEPOSITED HETEROJUNCTION OF CuO/Cu<sub>2</sub>O

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The structures and the electronic band states of the electrodeposited thin film CuO/Cu<sub>2</sub>O heterojunction have been studied by means of the X-ray diffractions (XRD) and the X-ray absorption spectra (XAS) with different grazing angles of the incident X-ray beam using the synchrotron radiation. The heterojunction of about 2 µm consists of n-type Cu<sub>2</sub>O (~1 µm) and p-type CuO (~1 µm) thin films bi-layer. Scanning electron micrographs (SEMs) show the existence of two different polycrystalline grain layers and the XRD reveals that the different grain layers are high quality CuO-type and Cu<sub>2</sub>O-type structures respectively. Photoactive performances of the Ti/CuO/Cu<sub>2</sub>O/Au heterojunction are V<sub>oc</sub> of ~210 mV and J<sub>sc</sub> of ~310 mA/cm<sup>2</sup>. It reveals that the Cu<sub>2</sub>O grains are grown from the surfaces of the CuO polycrystalline grains and make very good contact with the CuO grains. It is found that the XAS of CuO/Cu<sub>2</sub>O heterojunction are convoluted independently by X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structures (XANES) spectra of the Cu<sub>2</sub>O and CuO grains, depending on the grazing angles. Present study reveals that bottom of the conduction band (Cu-4p\pi) of the Cu<sub>2</sub>O in the CuO/Cu<sub>2</sub>O heterojunction reduces by 0.57 eV relative to the Ti/Cu<sub>2</sub>O ohmic contact.

## INTRODUCTION

Copper oxides are available in two stable forms, cuprous oxide (Cu<sub>2</sub>O) and cupric oxide (CuO). These two oxides have two different colours, crystal structures and physical properties. Both oxides are being studied as possible candidates for photovoltaic applications because of their favourable electrical and optical properties. Cu<sub>2</sub>O is a semiconductor having a band gap of 2 eV [1, 2] and a cubic crystal structure with lattice constant of 4.27 [3, 4]. On the other hand CuO is a p-type semiconductor having a band gap of 1.2 eV [1] and a monoclinic crystal structure with lattice constants a of 4.6837 Å, b of 3.4226 Å, c of 5.1288 Å, and β of 99.54° [3]. Among the various Cu<sub>2</sub>O deposition techniques [5-9], electrodeposition [4, 10] is an attractive because of its simplicity, low cost and low temperature process and on the other hand can be easily adjusted the composition of the material leading to changes in physical properties. Although fabrication of Cu<sub>2</sub>O and CuO based heterojunctions with other materials have been reported [11-14], investigations of CuO/Cu<sub>2</sub>O heterojuction are very limited in the literature because of inability to grow

n-type Cu<sub>2</sub>O (or CuO). In recent years, considerable attention has been given on developing CuO/Cu<sub>2</sub>O heterojunction after Siripala et al. [15] reported the possibility of growing n-type Cu<sub>2</sub>O. We reported growth of n-type Cu<sub>2</sub>O by potentiostatic electrodeposition [4], electronic structures and local structures for Cu ions of electrodeposited Cu<sub>2</sub>O [16] and annealing effects of electrodeposited Cu<sub>2</sub>O [17]. In the present paper, optoelectronic properties, local structure around the Cu ions and electronic band states near Fermi level ( $E_F$ ) of p–CuO/n–Cu<sub>2</sub>O heterojunction have been reported.

#### EXPERIMENTAL

Electrodeposition of  $Cu_2O$  thin films on Ti substrate were carried out under potentiostatic condition of -200 mV vs saturated calomel electrode (SCE) in a three electrode electrochemical cell containing aqueous solution of 0·1 M sodium acetate and 0·01 M cupric acetate [4]. The counter electrode was a platinum plate and reference electrode was SCE. Electrolytic solutions were prepared with de-ionized water and reagent grade chemicals. Electrodeposition was carried out for 1 hour in order to obtain the film thickness of ~1  $\mu$ m in the flat surface of 10×15 mm<sup>2</sup>. Ti/Cu<sub>2</sub>O films were annealed at 500° C for 30 min in air for conversion into CuO on Ti substrate. The details of the preparation of p-type CuO thin films have been reported earlier [17]. In order to deposit Cu<sub>2</sub>O thin film on Ti/CuO, the electrodeposition was carried out under different potentiostatic conditions of -250 mV, -400 mV, and -550 mV vs SCE in the same electrolytic conditions which used to deposit Cu<sub>2</sub>O on Ti substrate [4]. The surface morphology, the optoelectronic properties, the structures and the electronic band states of the electrodeposited CuO/Cu<sub>2</sub>O heterojunction were determined by SEMs, dark and light current voltage measurements, XRD, and XAS (EXAFS and XANES).

### **RESULTS AND DISCUSSION**

Figure 1 shows SEMs of Cu<sub>2</sub>O films deposited on Ti/ /CuO at -250 mV, -400 mV, and -550 mV vs SCE. Figure 1a shows the cubic shaped polycrystalline grains on CuO film, while Figure 1b and 1c show that the amount of Cu<sub>2</sub>O increases with increasing the deposition potential from -400 mV to -550 mV vs SCE. SEM results reveal that well covered Cu<sub>2</sub>O layer can be deposited on Ti/CuO under the potentiostatic condition of -550 mV vs SCE.

Dark and light current voltage measurements were obtained after depositing gold grid front contact to Ti/CuO/Cu<sub>2</sub>O heterojunction. As shown in Figure 2, Ti/CuO/Cu<sub>2</sub>O/Au heterojunction gave  $V_{oc}$  of ~210 mV and  $J_{sc}$  of ~310 µA/cm<sup>2</sup>. At the initial stage of the junction, diode shape and values of  $V_{oc}$  and  $J_{sc}$  are encouraging and improvement of the photoactive performance of the heterojunction will be subject for future investigations.

In order to find out the fabrication of CuO/Cu<sub>2</sub>O heterojunction on the Ti substrate, X-ray diffraction measurements were obtained for several grazing angles at room temperature, by using synchrotron radiations at the Pohang Light Source (2.5 GeV) of the Pohang Accelerator Laboratory (Korea). Figure 3 shows the X-ray diffraction spectrum of Ti/CuO/Cu<sub>2</sub>O heterojunction obtained by a 2 $\theta$  scan with step size  $2\theta = 0.03$  degree in the 2 $\theta$  range from 3.00° to 63.00°, where the grazing angle between the sample surface and the incident X-ray beam was 12.0 degree. X-ray wavelength was 1.5412 Å and its incident beam size was 0.1 mm in diameter. The diffraction pattern of the heterojunction shows the existence of both kinds of Cu<sub>2</sub>O-type and CuO-type structures. In Figure 3, the reflections belonged to Cu<sub>2</sub>O and CuO structures are denoted by "Cu<sub>2</sub>O" and "CuO", where the reflections resulted from the Ti substrate are denoted by "Ti". Thus, the fine peak profile of the reflections from the Cu<sub>2</sub>O and CuO grains and SEMs reveal that the formation of CuO/Cu<sub>2</sub>O heterojunction from the good quality CuO and Cu<sub>2</sub>O polycrystalline layers.

Grazing angle ( $\phi$ ) dependency of the X-ray diffraction patterns has been measured in order to study the structural properties of the thin layers formed by the CuO-types and Cu<sub>2</sub>O-type grains on the Ti substrate.







Figure 1. Scanning electron micrographs of electrodeposited  $Cu_2O$  on Ti/CuO electrodes at (a) -250 mV vs SCE, (b) -400 mV vs SCE and (c) -550 mV vs SCE.

The grazing angles were changed from 0.1 to 12.0 degrees and the data obtained are shown in Figure 4. The Ti peak of highest intensity at  $2\theta = 40.23$  degree is indexed by (0,1,1) and (1,1,1) reflections of hexagonal structure and were not observed below  $\phi \sim 2.0$  degree. On the other hand, the reflections of Cu<sub>2</sub>O-type and CuOtype structures were observed in all the grazing angles, though the reflections of Cu<sub>2</sub>O-type structure shows the different grazing angle dependence to those of the CuOtype ones. Figure 5 shows grazing angle dependency of (1,1,1) reflection of Cu<sub>2</sub>O, (1,1,-1) reflection of CuO, (1,1,1) reflection of Ti, and intensity ratio of Cu<sub>2</sub>O (1,1,1) and CuO(1,1,-1) reflections. The results suggest that  $Cu_2O$ -type grain layer can only be observed below  $\varphi =$ 0.1 degree. With increasing the grazing angle, CuO-type grain layer can be observed gradually, as Ti-reflections. The bulk structural information of Cu<sub>2</sub>O layer can be obtain for the grazing angles around 2.5 degree since it produces highest intensity of (1,1,1) reflection of Cu<sub>2</sub>O.



Figure 2. Dark and light current-voltage characteristics of Ti//CuO/Cu<sub>2</sub>O/Au heterojunction.



Figure 4. Grazing angle dependency of the X-ray diffraction patterns for the electrodeposited Ti/CuO/Cu<sub>2</sub>O heterojunction.



Figure 5. Grazing angle dependency of the (1,1,1) reflection of the Cu<sub>2</sub>O, (1,1,-1) reflection of the CuO structure, the (1,1,1) reflection of Ti and intensity ratio of Cu<sub>2</sub>O (1,1,1) and CuO (1,1,-1) reflections.



Figure 3. X-ray diffraction pattern of the electrodeposited Ti/CuO/Cu<sub>2</sub>O heterojunction at the grazing angle of 12 degree.

It reveals that it is possible to obtain optimum structural information within the Cu<sub>2</sub>O/CuO junction region in addition to the Cu<sub>2</sub>O, CuO, and Ti for the grazing angles slightly grater than 2.5 degree. Further it is found that the intensity ratio of the (1,1,1) reflection and (1,1,-1) reflection is approximately constant above  $\varphi = 5.0$  degree, in contrast to the intensity of the Ti-reflection. It shows that the bulk structural information of bi-layer (Cu<sub>2</sub>O and CuO) can be studied at the grazing angle 5 degree or greater. Thus, the X-ray diffraction patterns in Figure 4 suggest that the polycrystalline layers in Figure 1 consist of the good quality Cu<sub>2</sub>O-type and CuO-type polycrystalline structures.

Since the thin films of Ti/CuO/Cu<sub>2</sub>O/Au structure shows the electronic properties as shown in Figure 2, it can be considered that the bi-layer thin films consist of the good junction structure from Cu<sub>2</sub>O and CuO polycrystalline layers on Ti substrate. During the growth of CuO thin layer, the growing crystal axes of CuO grains were not oriented along a fixed angle to the Ti substrate plane, especially because of its monoclinic structure, as in Figure 1. Thus, it is suspected that the fine polycrystalline Cu<sub>2</sub>O are grown on the polycrystalline surface of CuO having many oriented directions during the electrodeposition in the aqueous solution of sodium acetate and cupric acetate. It can be considered that, in Figure 1, the deposition potential of -550 mV vs SCE is a more suitable potentiostatic condition to grow Cu<sub>2</sub>O on Ti/CuO in order to fabricate CuO/Cu<sub>2</sub>O heterojunction. Very thin Au grid consists of  $1 \times 8 \text{ mm}^2$  rectangles, was deposited on Ti/CuO/Cu<sub>2</sub>O by using a plasma vaporization technique in order to obtain front contact to CuO/Cu<sub>2</sub>O heterojunction. Au and Ti substrate were used as front and back contact to the CuO/Cu<sub>2</sub>O heterojunction for I-V characterization.

In order to study the structural deformation localized around Cu ions and the partial electronic band states of Cu ions in the electrodeposited semiconductor bi-layer thin films of CuO/Cu2O heterojunction, measurements of XAS at the Cu-K edge for the bi-layer thin film structure were carried out. The XAS, including XANES and EXAFS, were measured near the Cu-K edge for the electrodeposited bi-layer thin films, by using synchrotron radiation at the Pohang Light Source (2.5 GeV). Double crystal monochromators of Si (1,1,1)gave an energy resolution  $\Delta E$  to be less than about 0.2 eV in the respective measurements for the XAS near the Cu-K edge. The incident X-ray photons  $(I_0)$  were detected with an ionic chamber set in front of the thin film, and the X-ray fluorescence photons  $(I_{\rm F})$  emitted from the specimen surface were simultaneously detected with an X-ray fluorescence detector (Canberra Planar Silicon detector; PD3000). During measurements of the XAS, the surface of the thin films was always set with a respective grazing angle from 0.3 to 10.0 degrees to the incident X-ray beam, of which a size was about 5 mm in horizontal and 0.2 mm in vertical to the electron orbit of the accelerator.



Figure 6. Oscillating amplitudes  $I_F/I_o$  of the X–ray absorption spectra of the bi-layer thin film of the Ti/CuO/Cu<sub>2</sub>O heterojunction at  $\phi = 0.3$  to 10.0 degrees and of the electrodeposited Cu<sub>2</sub>O and CuO thin films, in addition to the calculated one of (0.5Cu<sub>2</sub>O + 0.5CuO), inset shows grazing angle dependency of the X–ray absorption spectra of the bi-layer thin film of the Ti/CuO/Cu<sub>2</sub>O heterojunction, taken at 300 K.

In the present investigations, software programs of *Artemis* and *Athena* were used to analysis the XAS data. The XANES spectra were obtained by subtracting a smooth background from the XAS after selecting two energy points in the pre-edge region of the XAS, while the EXAFS spectra were automatically obtained by a spline treatment after selecting a high-energy region above the X-ray absorption thresholds ( $E_0$ ). Self absorption corrections for the EXAFS spectra were automatically calculated using the *Athena* software program according to the Booth algorithm [18] even though correction is very small for thin films.

Inset of Figure 6 shows the XAS of the electrodeposited bi-layer thin films of the Ti/CuO/Cu<sub>2</sub>O heterojunction in the region of 8800 to 9430 eV near the Cu-K edge. The data were obtained at 300 K. It is found that the XAS are slightly modified from 9000 to 9200 eV. The behavior is also confirmed in Figure 6, where the partial XAS are expanded. The electrodeposited CuO/Cu2O thin films include Cu ions sited at different structures of Cu<sub>2</sub>O-type and CuO-type. The spectra of Cu-XAS result from a convoluted spectra induced by interference between the X-ray photoelectron waves emitted by X-ray absorbing Cu ions and the backscattering waves of its surrounding ions for both structures. Thus, the grazing angle dependency of the XAS in Figures 6 suggests that the incident X-ray beam penetrated the bi-layer of Cu<sub>2</sub>O and CuO grains by the different path distance. We consider that the measurements done at  $\varphi = 0.3$  and 0.5 degrees give mainly the XAS of Cu<sub>2</sub>O-type grainlayer, which was the up-part of the bi-layer thin films on the Ti substrate, as shown in Figures 4 and 5. To verify expectation, we compare the oscillating amplitudes  $I_{\rm F}/I_{\rm o}$  of the XAS obtained at  $\varphi = 0.5$  and 3.0 degrees with the observed XAS of electrodeposited thin films of Cu<sub>2</sub>O and CuO. The results are shown in Figure 6. Thus, it is found that the XAS obtained with  $\varphi = 0.5$ degree is not similar with the ones of Cu<sub>2</sub>O and CuO. This means that the XAS obtained with  $\varphi = 0.5$  degree is the convoluted spectra induced by the Cu<sub>2</sub>O and CuO structures, as shown in Figures 4 and 5. In Figure 6, the XAS data denoted by gray solid line was obtained by mathematical calculation  $0.5(Cu_2O - XAS) + 0.5(CuO-$ XAS). The calculated spectrum is very similar with the XAS obtained with  $\varphi = 0.5$ . However, the XAS obtained with  $\phi > 0.5$  degree could not be analyzed by a simple mathematical convolution of both XAS of Cu<sub>2</sub>O and CuO structures. This suggests that the complexity of the XAS depends on the different penetration lengths of the incident X-ray beam into the bi-layer grains of Cu<sub>2</sub>O and CuO. Thus, it is considered that the XAS of the Ti/CuO/ Cu<sub>2</sub>O heterojunction give information for the electronic band states of Cu ions in the conduction and valence bands near the Fermi level.

XAS of  $CuO/Cu_2O$  hetrojunction with different grazing angles have been further compared by studying corresponding Fourier transformations of the oscillating

EXAFS spectra. Fourier transformations were obtained using the Artemis and Athena software. Before obtaining the Fourier transformation, |F(R)|, X-ray absorption threshold  $(E_0)$  for Cu-K edges have been determined by differentiation of XAS curve near the X-ray absorption edges. Figure 7 shows the observed |F(R)| for the bi-layer thin film of Ti/CuO/Cu<sub>2</sub>O heterojunction at  $\varphi = 0.5$  and 3.0 degrees and for the electrodeposited Cu<sub>2</sub>O and CuO thin films with calculated one of (0.5  $Cu_2O + 0.5 CuO$ ), where the abscissa is a radial distance (R(Å)) from a X-ray absorbing Cu ion (CuA) to its surrounding cations and anions. The observed and calculated |F(R)| of the electrodeposited Cu<sub>2</sub>O and CuO thin films were already reported [17]. Thus, it is further confirmed that the |F(R)| obtained at  $\varphi = 0.5$  and 3.0 degrees are not similar with that of Cu<sub>2</sub>O structure and CuO one, but more complex. Further, comparison between the |F(R)|of the bi-layer thin film obtained at  $\varphi = 0.5$  degree and



Figure 7. Amplitudes |F(R)| obtained from the Fourier transformation of the EXAFS spectra of the bi-layer thin film of the Ti/CuO/Cu<sub>2</sub>O heterojunction at  $\varphi = 0.5$  and 3.0 degrees and of the electrodeposited Cu<sub>2</sub>O and CuO thin films and the calculated one of (0.5 Cu<sub>2</sub>O + 0.5 CuO).



Figure 8. XANES spectra of the Ti/CuO/Cu<sub>2</sub>O heterojunction at  $\phi = 0.3$  and 10.0 degrees and of the electrodeposited Cu<sub>2</sub>O and CuO thin films, in addition to the calculated one of (0.5 Cu<sub>2</sub>O + 0.5 CuO).

the calculated one of  $(0.5Cu_2O + 0.5CuO)$  suggests that the |F(R)| of the bi-layer thin film is also convoluted by those of the Cu<sub>2</sub>O and CuO structures, as in Figure 6. Furthermore, this indicates that the XAS give interesting information of the electronic band states for the CuO/ Cu<sub>2</sub>O heterojunction.

It is known that a XANES spectrum in the region of about -50 to 40 eV around X-ray absorption edge gives partial electronic band states sited in the valence band and the conduction band near an  $E_{\rm F}$ . Figure 8 shows the XANES spectra in the region of 8970 to 9005 eV for the Ti/CuO/Cu<sub>2</sub>O heterojunction obtained at  $\varphi$  from 0.3 to 10.0 degrees and for the observed electrodeposited Cu<sub>2</sub>O and CuO thin films with calculated one of (0.5Cu<sub>2</sub>O + 0.5CuO). It is found in Figure 8 that there are three XANES peaks above X-ray absorption threshold  $(E_0)$ for Cu-K edges, appearing at about 8982.0 (P1), 8985.8 (P2), and 8996.0~8997.5eV (P3). In order to study these XANES peaks, the XANES spectra of Ti/CuO/Cu<sub>2</sub>O heterojunction and of the electrodeposited Cu<sub>2</sub>O and CuO thin films were compared. As described before, the EXAFS spectra in Figure 6 and the |F(R)| in Figure 7 for XAS obtained at  $\varphi = 0.5$  degree adequately agreed the calculated one of  $(0.5Cu_2O + 0.5CuO)$ . The agreement is also confirmed in the energy region of the XANES spectra in Figure 8. The fact suggests that the XANES spectra certainly give the convoluted information for the electronic band states of the Ti/CuO/Cu<sub>2</sub>O heterojunction with the respective grazing angles. It is further found that the P1 and P2 XANES peaks correspond to the XANES peaks denoted by PA and PB of the electrodeposited Cu<sub>2</sub>O and CuO thin films, respectively.

An electronic dipole transition usually occurs only between two electronic bands having a difference of quantum numbers  $(\ell, j)$ ;  $\Delta \ell = \pm 1$  and  $\Delta j=0, \pm 1$ . We consider that the PA and PB XANES peaks correspond to unoccupied bands of Cu-4p $\pi$  in the conduction band, while the P3 peak to a band of Cu-4p $\delta$ , as regarding the electronic band structures of Cu<sub>2</sub>O and CuO reported by Ghijsen et al. [3] and Ching et al. [19] and the electronic dipole transition. Thus, we suspect that the P1 and P2 XANES peaks correspond to the PA and PB respectively. However, the P1 peak sites at the lower energy than that of the PA peak, while the P2 peak at the same energy with that of the PB peak. We consider that the Cu-4p $\pi$ band of the Cu<sub>2</sub>O structure is slightly modulated in the Ti/CuO/Cu<sub>2</sub>O heterojunction.

In order to study the relative energy-sift ( $\Delta E$ ) among the Cu-4p $\pi$  bands of Cu<sub>2</sub>O thin film, CuO thin film, and the Ti/CuO/Cu<sub>2</sub>O heterojunction, energy difference of the Cu-4p $\pi$  bands was calculated after smoothing the XANES spectra. The results are shown in Figure 9. When  $\varphi = 3.0$  degree,  $\Delta E$  (PB–PA) = 3.34 eV,  $\Delta E$ (PB–P1)  $\approx \Delta E$  (P2–P1) = 3.91 eV, and  $\Delta E$  (PA–P1) = 0.57 eV. In the present investigations, we determined the X–ray absorption threshold ( $E_0$ ) for Cu-K edges of the electrodeposited Cu<sub>2</sub>O and CuO thin films, by differentiation of XAS curve near the X-ray absorption edges.  $E_0$  of Cu<sub>2</sub>O and CuO were about 8981.04 and 8983.82 eV, respectively.

Figure 10a shows a schematic drawing of the energy band states in the conduction and valence bands near  $E_{\rm F}$  of the Ti/Cu<sub>2</sub>O and the Ti/CuO, obtained in Figure 9. Thus, it is considered that the Fermi level approximately consists with a donor level of the Cu<sub>2</sub>O thin film and an acceptor level of the CuO thin film. In the present investigations, we found  $\Delta E$  (PB–PA) = 3.34 eV,  $\Delta E$  (PB–P1) = 3.91 eV, and  $\Delta E$  (PA–P1) = 0.57 eV. Figure 10b shows the CuO/Cu<sub>2</sub>O heterojunction, which has two ohmic contacts of Au to the Cu<sub>2</sub>O and Ti to the CuO. We also found  $\Delta E$  (P2–P1) = 3.91 eV. Since P2  $\approx$  PB in Figure 10, the energy level of P1 of the CuO/Cu<sub>2</sub>O heterojunction reduces by 0.57 eV to the one of the Ti/Cu<sub>2</sub>O ohmic contact.

The fact suggests that the energy level at the bottom of the  $Cu_2O$  conduction band closes to the Fermi level that is the donor level, when making the CuO// $Cu_2O$  heterojunction. P1 band reduction by 0.57 eV of



Figure 9. XANES spectra of the Ti/CuO/Cu<sub>2</sub>O heterojunction at  $\phi = 3.0$  degree and of the electrodeposited Cu<sub>2</sub>O and CuO thin films.



Figure 10. Schematic energy band states in the conduction and valence bands near the Fermi level a) for the  $Ti/Cu_2O$  and Ti/CuO ohmic contacts and b) the  $Ti/CuO/Cu_2O/Au$  heterojunction.

CuO/Cu<sub>2</sub>O heterojunction suggests that the maximum possible open circuit voltage for the present CuO/ Cu<sub>2</sub>O heterojunction is ~ 280 mV ( $\Delta E$  (PA-P1)/2) when it expose to the light. Experimentally observed  $V_{oc}$  from I-V characteristics is 210 mV and it is very closer value suggested by electronic band states of CuO/Cu<sub>2</sub>O heterojunction. It is planning to enhance the photoactivity of the CuO/Cu<sub>2</sub>O heterojunction by improving the  $\Delta E$  (PA-P1) adjusting the heterojunction fabrication conditions.

#### CONCLUSION

In the present investigations, structural and electronic properties of the electrodeposited Ti/CuO/Cu2O heterojunction have been studied by means of the X-ray diffractions and the X-ray absorption spectra using the synchrotron radiation. The measurements were carried out with the small grazing angles of the incident X-ray beam. In conclusion, our study reveals that it is possible to electrodeposite Cu<sub>2</sub>O on Ti/CuO at the deposition potentials of -550 mV vs SCE in an acetate bath in order to fabricate CuO/Cu<sub>2</sub>O heterojunction. The SEMs and the photoelectric properties of the Ti/CuO/Cu<sub>2</sub>O heterojunction suggested that the Cu<sub>2</sub>O grains are grown from the surfaces of the CuO polycrystalline grains and make the good junction with the CuO grains. XRD reveals that CuO/Cu<sub>2</sub>O heterojunction consists of structurally high quality Cu<sub>2</sub>O and CuO grains layers. XAS of CuO/ Cu<sub>2</sub>O heterojunction are convoluted independently by EXAFS and XANES spectra of the Cu<sub>2</sub>O and CuO grains, depending on the grazing angles. The XANES spectra reveal that bottom of the conduction band of the  $Cu_2O$  in the CuO/Cu<sub>2</sub>O heterojunction reduces by 0.57 eV relative to the Ti/Cu<sub>2</sub>O ohmic contact. This result suggests that the maximum possible open circuit voltage for the present electrodeposited CuO/Cu<sub>2</sub>O is ~ 280 mV.

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