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Cu₂O-Based Homostructure Fabricated by Electrodeposition Method

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The Cu₂O-based homostructure thin film was successfully fabricated on FTO glass substrate using conventional electrodeposition method. Prior to the *p*-Cu₂O thin film deposition, cyclic voltammetry (CV) measurement was carried out in order to obtain optimum deposition parameter. Based on the CV result, *p*-Cu₂O thin film was deposited on *n*-Cu₂O with deposition potential of -0.4 V vs Ag/AgCl, solution temperature of 40 °C and pH 12.5, respectively. The deposition time was varied and it was found that the optimum deposition time for Cu₂O-based homostructure thin film was 2 h. Structural, morphological, and optical properties were characterized using X-ray diffraction, field emission-scanning electron microscope and ultraviolet and visible absorption spectroscopy, respectively. The successful fabrication of homostructure was confirmed using photoelectrochemical measurement.

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1. Introduction

The development of solar cell has attracted increasing attention as an effective, sustainable and another greenhouse energy source due to the pollution problem by carbon dioxide from fossil fuels renewable source energy [1]. The typical material for solar cell is wafer silicon, which demonstrated conversion of solar energy to electricity. However, the high cost material and processing in wafer silicon modules have forced the inventors to create another photovoltaic cell. In order to obtain new photovoltaic cell which more inexpensive, simple and able to produce high efficiency and long lifetime, there has been a regeneration of interest in solar cell based on Copper Oxide (Cu₂O) as an active layer because this metal-oxide semiconductor presents several essential characteristics that useful for the production of solar cell [2–4]. Over past three decades, Cu₂O thin film has been fabricated with metal/Cu₂O Schottky junction and *p*–*n* heterojunction such as *n*-CdO/*p*-Cu₂O, *n*-ZnO/*p*-Cu₂O and *n*-ITO/*p*-Cu₂O. The conversion efficiency of Cu₂O fabrication as an active layer is around 2% with *p*–*n* heterojunction structure [5]. This low efficiency is believed due to heterojunction layer which confronted improper band alignment and lattice mismatch between the Cu₂O crystal structures with other different materials. The other defects at the interface also produce conditions that promote recombination and loss of performance [6]. Thus, *p*–*n* ho-

mojunction of Cu₂O is introduced as the best way for the growth of (111)-oriented Cu₂O layer as there is no interface strain occur between the same material of Cu₂O thin film [6, 7]. However, it is not easy to obtain *n*-Cu₂O since Cu₂O is naturally *p*-type semiconductor [2, 3]. It was reported that, the polarization of Cu₂O could be adjust by manipulating the pH solution and could be executed only using electrodeposition method [4]. For these reasons, there are lack of informations and research were reported until to date.

In this study, *n*- and *p*-Cu₂O thin film was fabricated using electrodeposition method in acidic and alkaline electrolytes, respectively. Firstly, *n*-Cu₂O was fabricated on FTO glass substrate and followed by *p*-Cu₂O layer. The homostructure properties before and after deposition of *p*-Cu₂O thin film were characterized in order to obtain optimum parameters to increase the conversion efficiency solar cell.

2. Experimental procedure

Fabrication of Cu₂O homostructure thin film on FTO substrate was carried out using conventional electrodeposition method. Copper(II) acetate, lactic acid and potassium hydroxide were used as based solution. Firstly, the *n*-Cu₂O thin film was fabricated on FTO substrate using acidic electrolyte. The deposition was performed at 60° and -0.125 V vs Ag/AgCl for 30 min. Prior to the *p*-Cu₂O deposition, cyclic voltammetry (CV) measurement was done in order to optimize the deposition parameter. The CV measurement was carried out at scan rate of 5 mV/s with potential range from $+0.5$ until -1.0 V vs Ag/AgCl. After that, *p*-Cu₂O thin film

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was immediately stacked on the n -Cu₂O layer at pH solution of 12.5. The deposition was done at 40° and potential value of -0.4 V vs Ag/AgCl. The deposition time was varied at 1 h and 2 h. The properties of homostructure was investigated using X-ray diffractometer (XRD) (Bruker, Model D8 Advance), field emission-scanning electron microscope (FE-SEM) (JEOL, Model JMS-7600F) and ultraviolet-visible absorption spectroscopy (UV-Vis) (Shimadzu, Model UV 1800), respectively. Polarization of the homostructure was investigated using photoelectrochemical measurement (USHIO Optical Modulex) with sodium hydroxide as an electrolyte.

3. Results and discussion

Prior to the deposition of p -Cu₂O, cyclic voltammetry (CV) measurement was performed to obtain optimum deposition parameter. As seen in Fig. 1, two cathodic reduction regions were clearly observed. The first region occurred from -0.30 V until -0.45 V vs Ag/AgCl and second region around -0.45 V vs Ag/AgCl onwards. The first peak was attributed to reduction reaction of Cu²⁺ to Cu⁺ and hence to Cu₂O. Then, the second peak endorsed to reduction reaction of Cu⁺ to Cu which is metallic copper formation. These findings were corresponding to previous study by M. Izaki et al. which concluded that deposition of p -Cu₂O thin film should be in the range of cathodic region [8]. Wang et al. [9] also stated that solution with pH more than 9 was p -Cu₂O thin film.

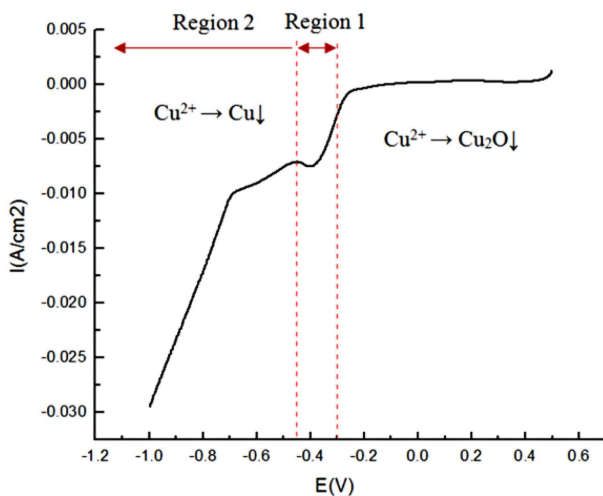


Fig. 1. Cyclic voltammetry of p -Cu₂O thin film.

3.1. Structural characterization

The structural properties of Cu₂O thin film was characterized using XRD. Various peaks detected at 36.45, 42.35, 61.44 and 73.59° corresponding to the [111], [200], [220] and [311]-Cu₂O orientation consistent with the previous finding by Fariza and Izaki et al. [3, 8]. Based on the result, the n -Cu₂O possessed [111] preferred orientation. All the peaks was not changed and remain almost

the same after deposition of p -Cu₂O for 1 h. When the deposition time increased from 1 h to 2 h, the amount of p -Cu₂O increased resulting in enhancement of [111] and other peaks of Cu₂O. There were no other peaks corresponding to metallic copper or other impurities were observed on the XRD pattern. The XRD result are shown in Fig. 2.

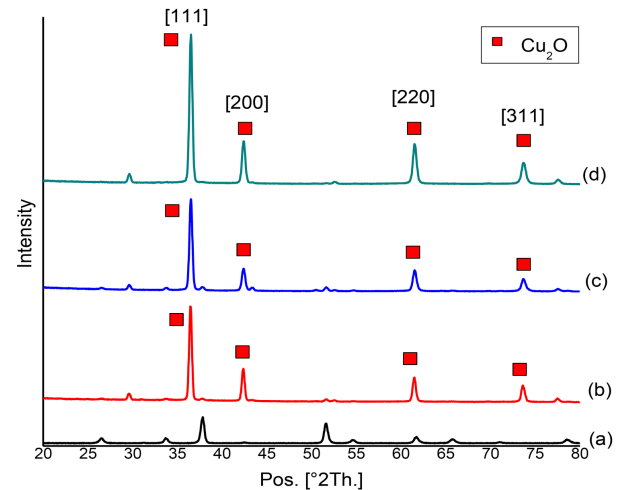


Fig. 2. XRD pattern for (a) FTO; (b) n -Cu₂O and homostructure with p -Cu₂O (c) 1 hour; (d) 2 hours deposition, respectively.

3.2. Morphological characterization

Besides, morphological properties was obtained using field emission-scanning electron microscope (FE-SEM) observation. Based on the findings, all the samples before and after deposition of p -Cu₂O thin film exhibited triangular with combination of pyramidal shape. This results was believed corresponding to [111]-plane of Cu₂O in structural properties and consistent with previous reported study [10]. It was proved that both acidic (pH 6.3) and alkaline (pH 12.5) electrolytes facilitate contribution a stable condition for the growth of a Cu₂O thin film [4]. Basically, the n -Cu₂O thin film grew in pyramid shaped with well-defined boundaries individually as seen in Fig. 3a. It was observed that the small grains agglomerated to form larger and denser grains thereby the surface was covered well with more number of pyramid shaped grains after deposition of p -Cu₂O thin film as shown in Fig. 3b and c. Thus, more crystallites agglomerate to forms grains and the surface mobility enhanced indirectly [5, 10]. These results were good agreement with the highest intensity of p -Cu₂O thin film for pH 12.5 at 2 h. The FE-SEM images for n -Cu₂O before and after deposition of p -Cu₂O at 1 h and 2 h are shown below.

3.3. Optical characterization

The optical absorption study of Cu₂O thin film was carried out in the wavelength range between 300 nm and 800 nm at room temperature. Based on the result shown in Fig. 4a and b, there are two absorption

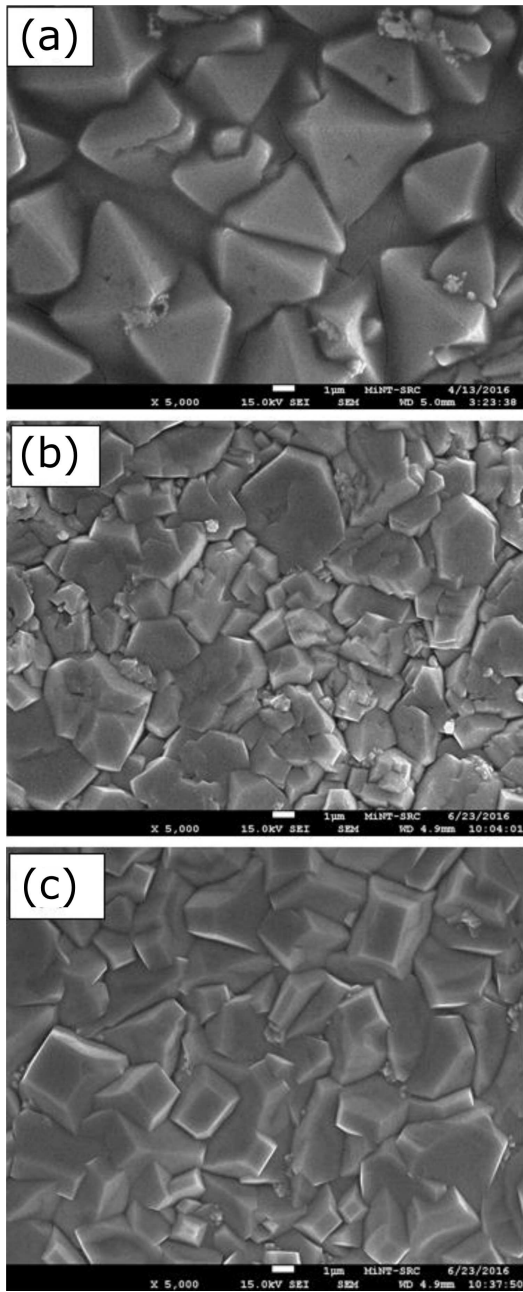


Fig. 3. FE-SEM images for (a) *n*-Cu₂O and homostructure with *p*-Cu₂O deposited at (b) 1 h, (c) 2 h, respectively.

stages was observed for *n*-Cu₂O and after deposition of *p*-Cu₂O for 1 h, which believed corresponding to the Cu₂O and FTO absorption edge, respectively. However, only one absorption edge was seen for the sample prepared at 2 h that shown in Fig. 4c. It believed that this changes was due to homogeneity surface of *p*-Cu₂O thin film. The sample showed very good absorbance at wavelength about 650 nm and had a good agreement with the wavelength reported earlier by Izaki et al. [8]. Besides, the absorbance coefficient satisfies the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ for a direct bandgap material and the bandgap value obtained was 1.8 eV.

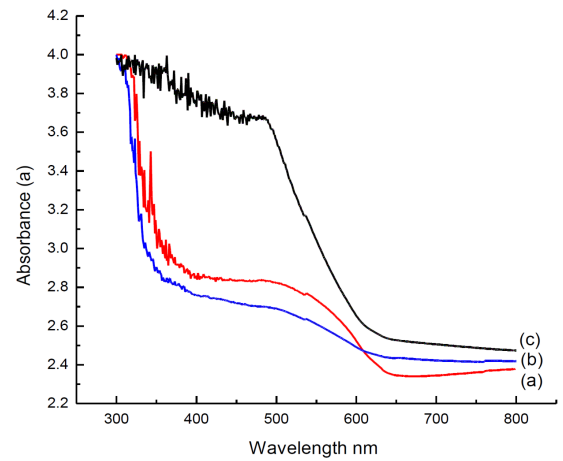


Fig. 4. Absorbance spectrum for (a) *n*-Cu₂O and homostructure with *p*-Cu₂O (b) 1 h, (c) 2 h deposition, respectively.

3.4. Photoelectrochemical measurement

To verify the successful deposition of *p*-Cu₂O on *n*-Cu₂O, photoelectrochemical (PEC) measurement was performed for both layers. Firstly, the photocurrent behavior of Cu₂O with pH 6.3 was measured and followed by Cu₂O deposited at pH 12.5. The result was shown in Fig. 5. PEC process was carried out by turning ON and OFF the light for time interval of 5 s, respectively and measured for 60 seconds. Based on the results, Cu₂O deposited at pH 6.3 exhibited a typical anodic photocurrent

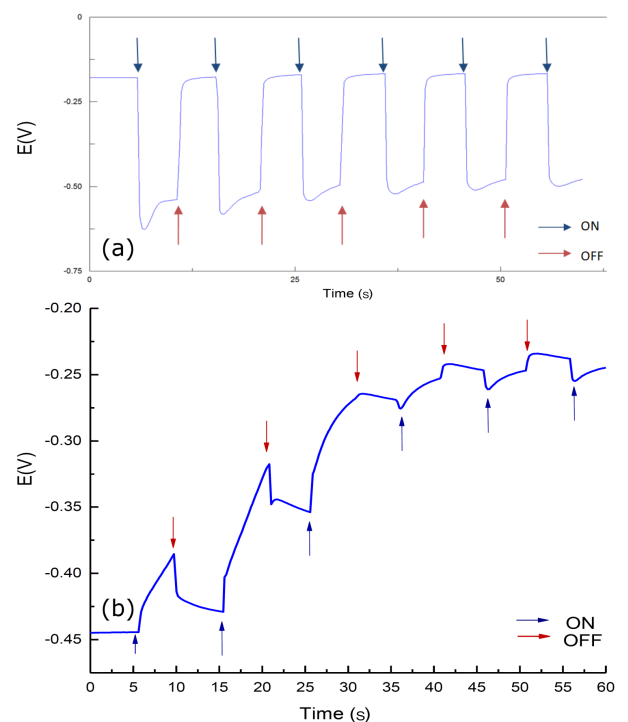


Fig. 5. Photocurrent-voltage for (a) *n*-Cu₂O and (b) homostructure with *p*-Cu₂O deposited at 2 h, respectively.

response for n -Cu₂O which the voltage dropped after illuminating for 5 s as seen in Fig. 5a. Meanwhile after deposition of p -Cu₂O thin film, the voltage had increased after illumination corresponding to cathodic photocurrent response for p -type behavior as shown in Fig. 5b. This indicated that the p -Cu₂O has been successfully deposited on n -Cu₂O and a p - n homojunction was performed [9]. The anodic and cathodic photocurrent for both types of Cu₂O thin films were related to energy band edge bending diagrams of the p - and n -Cu₂O thin film/electrolyte system. For anodic photocurrent of n -Cu₂O thin film, the electron was gained energy and excited from the valence to the conduction band when light was switched on. Then, the electron was drifted from the electrolyte to the Cu₂O thin film. As more electrons were drifted to Cu₂O thin film, the electrons accumulation had caused the potential value of the Cu₂O thin film dropped to more negative value. When the light was switched OFF, the value of the potential will return to the original state. Meanwhile, for cathodic photocurrent of p -Cu₂O thin film/electrolyte interface, the excited electrons at the thin film were transferred to the electrolyte, due to the excess of electrons in the thin film compared to the electrolyte. Electrons from both thin films to the electrolyte and hole to the bulk of semiconductor caused the potential increased when the light was illuminated on the sample. Thus, a net positive photo-potential difference and cathodic photocurrent was displayed in p -Cu₂O thin film.

4. Conclusion

In this study, the Cu₂O-based homostructure was successfully fabricated using electrodeposition method. It was found that the optimum parameters for fabrication of p -Cu₂O on n -Cu₂O were pH solution of 12.5, bath temperature of 40°, potential deposition of -0.4 V vs Ag/AgCl and deposition time of 2 hours. Several characterizations were carried out to acquire the properties for fabrication. As the result, fabricated Cu₂O-based homostructure exhibited high structural properties, homogenous morphology and excellent optical behaviour which believed to have high possibilities for better conversion efficiency of homojunction thin film fabrication.

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