



Figure A.1 Preparation flow chart of CuO nanowires by oxidation of copper plate.



Figure A.2 Preparation flow chart of CuO thin films by oxidation of copper thin films.



Figure A.3 Preparation flow chart of ZnO target.



Figure A.4 Preparation flow chart for synthesis ZnO nanobelts and nanowires by RF sputtering technique.



Figure A.5 Preparation flow chart of DSSC based ZnO.

Appendix B

 l_0

L

Η

Thickness calculation of evaporation

Figure B.1 Schematic diagram of evaporation source to substrate.

m

The mass of starting materials is m. The distance between substrate and starting materials is H and the substrate size of L. the thickness of evaporated (l_0) films can calculate by

 $V_{start} = V_{thin film}$ (B.1). $V_{start} = Area \cdot Thickness$ (B.2). $V_{start} = 4\pi H^2 \cdot l_0$ (B.3).

$$\frac{\rho}{V} = 4\pi H^2 \cdot l_0 \tag{B.4}.$$

$$\therefore \qquad l_0 = \frac{m}{4\pi\rho H^2}$$
(B.5)

Figure B.2 The relationship of thickness with length of substrate.

0 *L/H*

In this case, we calculated the thickness on substrate in a part of sphere but the real substrate is flat. Thus, the relationship of thickness when the length of substrate was changed can be write as

$$U = \frac{m \left\{ \frac{1}{1 + (L/H)^2} \right\}^2}{\pi \rho H^2}$$

(B.6).

- *l* is source thickness of deposited film
 m is total deposited mass
 ρ is density of material
 L is distance between the centre of substrate and the point where the thickness is calculated
- *H* is the distance between source and substrate

The next approximation, we calculate thickness by

$$\frac{l}{l_0} = \frac{1}{\left[1 + (L/H)^2\right]^2}$$
(B.7).
The thickness decrease by 10% for *L=H/4*.

Appendix C

PAPER PUBLICATIONS

Paper Publications

 Paper I
 Ethanol sensing properties of CuO nanowires prepared by an oxidation

 reaction

Paper IICuO Nanostructure by Oxidization of Copper Thin Films

 Paper III
 Copper oxide thin film and nanowire as a barrier in ZnO dye-sensitized solar cells

Paper I



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Ethanol sensing properties of CuO nanowires prepared by an oxidation reaction

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Abstract

The ethanol sensing properties of CuO nanowires prepared by oxidation reaction of copper plate have been examined. The characterization of CuO nanowires by FE-SEM, EDS, and TEM revealed diameters of 100-400 nm and a monoclinic structure with a growth direction along $\langle 1 1 0 \rangle$ direction. The ethanol sensing characteristics of CuO nanowires were studied at ethanol concentrations of 100-1000 ppm and working temperatures of 200-280 °C. An increase of resistance was observed under an ethanol vapor atmosphere due to the p-type semi-conducting property of CuO. It was found that the sensitivity, the response and the recovery time depended on the working temperatures and also ethanol 240 °C with a response and recovery time of 110 and 120 s, respectively.

Keywords: B. Electron microscopy; E. Sensors

1. Introduction

Copper oxide (CuO) is a metal-oxide semiconductor with a narrow band gap of 1.2 eV and is one of the few metal-oxide semiconductors that exhibit p-type conductivity. Also, it is an important building block of most high-temperature superconductors. Recently, nanostructures of semiconductors have caught attention due to the unique property of having a huge surface-to-volume ratio which is expected to enhance the performance of the devices based on semiconductor nanostructures.

CuO nanostructures can be synthesized by various growth techniques such as thermal evaporation, thermal decomposition, sol-gel, and oxidation reaction [1-8]. An oxidation reaction technique is one of the more practical and simple ways of synthesis [8]. CuO can be used for a wide range of applications such as photoconductive, photothermal, catalysis and gas sensor [9-13]. For gas sensor application, it is interesting to investigate the effect of CuO nanostructure, which has a huge surface-to-volume ratio, on gas sensing properties. Thus, in this work, the

ethanol sensing properties of CuO nanowires prepared by oxidation reaction are examined. The ethanol sensing properties were studied for various ethanol concentrations and working temperatures.

2. Experimental method

The commercial grade copper plate with thickness of 0.1 mm was cut and cleaned by alcohol in an ultrasonic bath for 2 min and dried at room temperature. The copper plate was loaded into a center of a tube furnace at 600 $^{\circ}$ C at normal atmosphere for oxidation reaction. The oxidation reaction [8] follows in Eqs. (1) and (2).

$$4Cu + O_2 \rightarrow 2Cu_2O \tag{1}$$

$$2\mathrm{Cu}_{2}\mathrm{O} + \mathrm{O}_{2} \to 4\mathrm{Cu}\mathrm{O} \tag{2}$$

After oxidation reaction for 6 h, the copper plate was taken out of the furnace and immediately cooled down in air. The colour of the copper plate changed to black after oxidation reaction. It has been reported that the colour of CuO, Cu_2O and Cu are black, red and copper, respectively [8]. Therefore, the black product that

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Fig. 1. Schematic diagram of a sensor fabricated from CuO nanowires and a layer of CuO.

was separated out from the copper plate after being taken from the furnace was CuO from appeared colour. The CuO was investigated by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F) for morphology, energy dispersive spectroscopy (EDS) for chemical composition, and transmission electron microscopy (TEM, JEOL JEM-2010 operating at 200 kV) for the crystal structure. The black product, CuO, was separated from the copper plate for fabrication of ethanol sensor as shown in the schematic diagram, Fig. 1. It should be noted that the black plate (black product) substance was composed of CuO layered with CuO nanowires. The black plate was cut into a square shape with dimensions of $5 \text{ mm} \times 5 \text{ mm}$ before silver paint was applied at the diagonal corners of the black square to be silver electrodes, sized 1 mm \times 1 mm. A heater for the ethanol sensor was made from a nickel-chromium coil and wound around an alumina plate, resistance 80 Ω , and placed beneath the CuO plate. Finally, copper wires were attached to the silver electrodes for resistance measurement to complete the ethanol sensor. The sensing properties were studied by observing the change of resistance in air and in ethanol ambiences of ethanol concentration of 100, 200, 500 and 1000 ppm, respectively, and at working temperatures of 200-280 °C. The response and the recovery characteristics were monitored and recorded via an interfaced personal computer.

3. Result and discussion

3.1. FE-SEM and TEM analysis

Fig. 2(a) and (b) shows FE-SEM top and cross-section view images, respectively of CuO plate (black product) separated



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Fig. 3. A bright-field TEM image superimposed with the corresponding SADP of the CuO nanowires.

from the copper plate after oxidation reaction. The nanowires having a diameter of 100–400 nm and the length of around several micrometers were observed. The result of EDS shown in Fig. 2(c) confirms that the black product is CuO layered with CuO nanowire.

A bright-field TEM image of the CuO nanowires is shown in Fig. 3 superimposed with the corresponding SADP. Three wire-like structures with diameter about 100 nm can be observed. The SADP shows a spot pattern indicating the single-crystalline property of the CuO nanowire with monoclinic structure. Also, the spots show line-streaking along [3 0 0] corresponding to the shape factor of the nanowires on the reciprocal lattice node. Trace analysis results suggest that CuO has the growth direction along $\langle 1 1 0 \rangle$ direction.



Fig. 4. The response and recovery curves of the CuO nanowires sensor at an ethanol concentration of 1000 ppm, working temperature of 200–280 °C.



Working temperature (°C)	Steady resistance (R_g, Ω)	Ethanol ambient resistance (R_a, Ω)	Sensitivity
200	5314	7749	1.4
220	4290	6302	1.5
240	3232	4690	1.5
260	2610	2925	1.1
280	2229	2428	1.1

3.2. Gas sensing properties

Fig. 4 shows the response and the recovery curves of ethanol sensors based on CuO nanowires being exposed to an ethanol concentration of 1000 ppm and working temperatures of 200–280°C. At the beginning, the measured resistance was steady in an ambient atmosphere. But when ethanol vapor was injected into the chamber, an increase of resistance was observed; and when ethanol vapor was removed, a decrease of resistance was observed. The increase of resistance under in ethanol vapor atmosphere is due to the p-type conductivity of CuO. It can be clearly seen from Fig. 4 that the characteristic of the sensor depends on the working temperature. It should be noted that the lower resistance of CuO nanowires at higher working temperatures is due to the common, semiconductor property of CuO.

The sensitivity, S_g , of the sensor is defined as R_g/R_a where, R_g is the electrical resistance of a sensor in ethanol-air mixed gases; and R_a is the electrical resistance of sensor in air. The sensitivity obtained for the CuO nanowire sensor at different working temperatures at the ethanol concentration of 1000 ppm is listed in Table 1. The highest sensitivity was obtained at the working temperature of 240 °C, suggesting this was the optimum working temperature. In addition, the response time and the recovery time also depended on the working temperature, in the range of 30–235 s and 60–245 s, respectively.

Fig. 5 shows the response and the recovery curves of ethanol sensors based on CuO nanowires when exposed to an ethanol



Fig. 5. The response and the recovery curves of the CuO nanowires sensor at ethanol concentration of 100–1000 ppm and working temperature of 240 $\,^\circ\text{C}.$

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concentration of 100–1000 ppm at the working temperature of 240 °C. It was found that the sensitivity only slightly depended on the ethanol concentration.

4. Conclusion

The ethanol sensors based on CuO nanowires were successfully fabricated. The CuO nanowires were prepared by an oxidation reaction of copper plate. From FE-SEM, EDS and TEM characterization, CuO nanowires exhibited diameters of 100–400 nm having a monoclinic structure with a growth along $\langle 1 1 0 \rangle$ direction. Moreover, the CuO nanowire sensor responded to ethanol vapor, exhibiting the optimum sensitivity of 1.5 to an ethanol vapor concentration of 1000 ppm with a working temperature of 240 °C, the response time of 110 s, and recovery time of 120 s. The CuO nanowires could be explored for gas sensor application.

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Paper II

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CuO Nanostructure by Oxidization of Copper Thin Films

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Keywords: CuO, nanostructure, thin films

Abstract. CuO nanostructures were synthesized by oxidizing copper thin films. The copper thin film was grown on alumina substrates by evaporation copper powder at pressure of 0.04 mtorr. The copper thin films were then oxidized 800, and 900°C for 12, 24 and 48 hr, respectively. The obtained CuO nanostructures were investigated by Energy Dispersive Spectroscopy (EDS), Field Emission Scanning Electron Microscope (FE-SEM) image, and X-Ray Diffraction (XRD). The diameter of CuO nanostructure is around 100-600 nanometers and it is depends on oxidation reaction time and temperature. These CuO nanostructures have a potential application for nanodevices such as nano gas sensor or dye-sensitized solar cells.

Introduction

Copper oxide (CuO) show p-type conductivity. CuO is grey-black in color with a monoclinic crystal structure and a band gap of 1.2–1.5 eV. Also, it is an important building block of most high-temperature superconductors. Recently, nanostructures of semiconductors have caught attention due to the huge surface-to-volume ratio which is expected to enhance the performance of the devices based on semiconductor nanostructures.

CuO nanostructures can be synthesized by various growth techniques such as thermal evaporation, thermal decomposition, sol-gel, and oxidation reaction [1-8]. An oxidation reaction technique is one of the most practical and simple ways of synthesis [8]. CuO can be used for a wide range of applications such as photoconductive, photothermal, catalysis and gas sensor [9-13]. In the past few years, the different morphologies of CuO have attracted more interest for practical application. Compared with nanoparticles, CuO whiskers are expected to exhibit remarkable optical, electrical, magnetic, and mechanical properties. In electrochemical field, few reports have indicated the application of cupric (cuprous) oxides as electrode materials in batteries [14-17].

In this work, we have fabricated CuO nanostructures by oxidizing copper thin films and the obtained CuO nanostructures were characterized by different technique.

Experimental

Copper thin films were prepared by the evaporation method. High purity (99.9%) Copper powder was placed in heating coil of 0.4 mTorr. The films were evaporated onto an alumina plate in a vacuum tube, the distance between the electric boat and the substrate was 7 cm. The temperature of substrates was kept at room temperature. The alumina substrates ($20\text{mm} \times 30 \text{ mm}$) were first cleaned by alcohol in an ultrasonic bath for 2 min and dried at room temperature. After thermal evaporation, the copper thin films were loaded into the central position of a tube furnace and heat to 800 and 900°C at normal atmosphere for oxidation reaction.

After oxidation reaction of 12, 24 and 48 hr, the colour of the copper thin films changed to black. The obtained black products were investigated by FE-SEM (JEOL JSM-6335F) for morphology, energy dispersive spectroscopy (EDS) for chemical composition, and X-ray diffraction for crystal structure.

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Results and Discussion



Figure 1. FE-SEM top view images of the CuO thin films (black product) after oxidation reaction of copper thin films

Fig. 1 (a)-(d) showed FE-SEM top view images of CuO nanostructure after oxidation reaction of the copper thin films at 800°C for 12 hr, 24 hr, 48 hr and at 900°C for 12 hr, respectively. The nanostructures with a diameter of 100-600 nm were observed. The size of nanostructure depends on oxidation reaction time and oxidation reaction temperature. The size of nanostructure increased as increasing oxidation reaction time and oxidation reaction temperature. The thickness of CuO thin films was observed to be around 1 μ m, as shown in the cross section FE-SEM image in Fig. 2.



Figure 2. Cross-section view of the CuO thin films after oxidation reaction

The EDS spectrum of the CuO thin films after oxidation reaction at 800°C 48 hr was shown in Fig. 3. The peaks in the EDS spectrum correspond to Al, Cu and O elements. The Al signal comes from the alumina substrate.



Figure 3. EDS spectrum of the CuO thin films after oxidation reaction at 800°C 48 hr



Figure 4. XRD pattern of the CuO thin films after oxidation reaction at 800°C 48 hr.

Fig. 4 showed the XRD pattern of the CuO thin films after oxidation reaction at 800°C 48 hr. The diffraction peaks at $2\theta = 35.32^{\circ}$, 37.92° , 61.40° , 66.64° and 68.32° can be assigned to the (111), (111), (113), (311) and (220) planes of crystalline CuO, respectively. These peaks matched with reported data for CuO (JCPDS 45-0937). The peaks at $2\theta = 29.36$ can be assigned to the (110) planes of crystalline Cu₂O. These peaks matched with reported data for Cu₂O (JCPDS 03-0839). The peaks at $2\theta = 52.68^{\circ}$ and 57.64° can be assigned to the (024) and (116) planes of crystalline Λl_2O_3 . These peaks matched with reported data for Λl_2O_3 (JCPDS 47-1771). The peaks at $2\theta = 43.48^{\circ}$ can be assigned to the (110) planes of crystalline Cu. These peaks matched with reported data for CuO (JCPDS 04-0836). The XRD results showed that the films were not in single phase, and CuO was the main oxidation product with a small amount of Cu, and Cu₂O. The observation of Cu₂O and CuO phase can be explained in terms of oxidation reaction as shown in Eq.1 and Eq.2.

$$\begin{array}{l} 4\text{Cu+O}_2 \rightarrow 2\text{Cu2O} \\ 2\text{Cu}_2\text{O+O2} \rightarrow 4\text{CuO} \end{array}$$

The Cu phase was observed due to the incomplete oxidation reaction.

Summary

The CuO nanostructures were successfully synthesized by oxidizing copper thin films which were prepared by an evaporation method. The characterization of CuO nanostructure by FE-SEM revealed a diameter of around 100-600 nanometers and it depended on the oxidation reaction time and temperature. CuO and Cu₂O phases observed from XRD pattern agreed with oxidation reaction

(1)(2)

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process. The CuO nanostructures that can be grown on substrate may found application for nanodevices such as nano gas sensor or dye-sensitized solar cells.

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Paper III

Thin Solid Films 517 (2009) 4741-4744



Copper oxide thin film and nanowire as a barrier in ZnO dye-sensitized solar cells

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1. Introduction

Dye-sensitized solar cells (DSSCs) are a new type of metal-oxide wide-band-gap solar cells composed of dye-modified wide band gap semiconductor photoelectrode [1], the dye molecules adsorbed on the surface of the wide band gap semiconductor photoelectrode, a counterelectrode and an electrolyte containing a redox couple between photoelectrode and counterelectrode. The major progress of DSSCs was made by the work of Grätzel et al. [1,2]. They have realized the promising results with power conversion efficiency up to 10.8% as reported several years ago [3]. Nowadays, the DSSC based on titanium dioxide (TiO2) is widely investigated. Recently, the investigation on Zinc oxide (ZnO) as an alternative photoelectrode has been intensively carried out due to its band gap, electron affinity, and electron injection efficiency which are nearly the same as TiO2. In addition, in ZnO electron lifetime is significantly higher and the recombination rate is lower than that of TiO₂. However, the power conversion efficiencies of DSSCs based on ZnO are lower than that of TiO₂ [4,5]. Bandaranayake et al. have studied DSSCs made from high band-gap oxide semiconductors TiO2, SnO2 and ZnO and found that DSSCs based on TiO₂ showed higher efficiency than those of ZnO and SnO2 [6]. Several methods have been applied to improve the power conversion efficiencies of ZnO DSSCs [7,8]. For example, Kakiuchi et al. improved dye-loading in ZnO photoelectrodes by the formation of mesoporous microstructure and obtained power conversion efficiency as high as 4.1% [7]. Bandara et al. have fabricated the p-n junction electrode for minimizing the charge recombination in DSSCs. They

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0040-6090/\$ - see front matter © 2009 Elsevier R.V. All rights reserved doi:10.1016/j.tsf.2009.03.027 found that the efficiency of the TiO₂ DSSC can be improved and they have observed an open circuit voltage of about 730 mV, a short circuit current of about 16.7 mA, a fill factor of 0.66, and a power conversion efficiency of 7.74% [9]. Also, Palomares et al. have reported a coating of nanocrystalline TiO₂ films with a thin overlayer of a second metal-oxide to control charge recombination dynamics in DSSCs and observed an increase in V_{OC} of up to 50 mV and a 35% improvement in overall device efficiency of DSSCs with Al₂O₃ overlayer [10].

Copper oxides (CuO) is a few p-type metal-oxide semiconductors with a narrow band gap of 1.2 eV and a monoclinic crystal structure. It has received much attention due to a wide range of potential applications



Fig. 1. Schematic diagram of DSSC structures with different photoelectrodes for ZnO/CuO layer.

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Summary of starting material :	ind preparation conditions of different	nhotoelectrodes for ZnO/CuO laver

Type of photoelectrodes	Starting material of CuO layer	Preparation technique	Preparation conditions	Heating time to remove PEG (h)	Heating time for CuO oxidation reaction (h)
ZnO/CuO thin film	Copper powder	Evaporation	Base pressure 5 × 10 5 Torr	1	6
ZnO/CuO nanowires	Copper powder	Screening	With binder of PEG 1:1 by weight	1	6
ZnO/CuO powder	CuO powder	Screening	With binder of PEG 1:1 by weight	1	-
ZnO	-	-		1	

such as photoconductive, photothermal, catalysis and gas sensor [11]. Thus, CuO could be used as p-type metal-oxide layer with n-type ZnO layer to form a barrier layer in order to control charge recombination dynamics and improve the performance of ZnO DSSCs. The CuO nanostructures such as nanowires, nanorods, and nanoparticle etc. can be synthesized by various growth techniques, such as thermal evaporation [12], thermal decomposition [13] and oxidation [14–16].

In this work, we have fabricated CuO layer as a barrier layer in order to control charge recombination dynamics in ZnO DSSCs. The CuO layer has the structure of CuO powder, nanowire and thin film. Then, the effect of CuO layer on photoelectrochemical characteristics has been investigated.

2. Experimental details

The DSSC structures used in this experiment are shown as schematic diagram in Fig. 1 with different photoelectrodes for ZnO/CuO layer. Three types of ZnO/CuO photoelectrode were used in this experiment: ZnO powder/CuO powder, ZnO powder/CuO nanowires and ZnO powder/CuO thin film as listed in Table 1 with starting material and preparation conditions. For ZnO powder/CuO powder, ZnO powder 99.9% size <1 µm (Aldrich) in polyethyleneglycol (PEG) solution, ZnO:PEG with 1:1 by weight stirring for 30 min and CuO powder paste was prepared by dissolving CuO powder 99% size <1 µm (Fluka) in PEG solution, CuO:PEG with 1:1 by weight stirring for 30 min. Copper powder paste was prepared by dissolving copper powder 99% size <75 µm (Aldrich) in PEG solution, copper:PEG with 1:1 by weight stirring for 30 min. ZnO powder paste and heated at 400 °C for 1 h under normal

atmosphere to remove PEG. For ZnO powder/CuO nanowires, Copper powder paste was used instead of CuO powder paste and heated at 400 °C for 1 h under normal atmosphere to remove PEG and at 400 °C for 6 h for oxidation reaction. Finally, the third photoelectrode, CuO thin film was prepared by oxidation reaction of copper thin film preparing by thermal evaporation of copper powder without substrate heating. The thermal oxidation of copper thin film was performed at 400 °C for 6 h under normal atmosphere. The morphology of photoelectrode was investigated by field emission scanning electron microscopy (FE-SEM).

Then, the photoelectrodes were soaked in Eosin-Y organic dye solution (0.04 g of Eosin Y, C₂₀H₆Br₄Na₂O₅, in acetone 100 cm³) for 24 h. The dye-loaded ZnO as photoelectrode and the Pt counterclectrode (0.5 mM hydrogen hexachloroplatinate (IV) hydrate, Cl₆H₂Pt₋aq, in acetone solution) were assembled into a sealed device using a hot-melted double layer parafilm (50 µm thick). The redox electrolyte (0.3 M Li + 0.03 M I₂ in polyethylene carbonate) was introduced into the inter-space between the photoelectrode and the counterelectrode through two predrilled holes on the side of the device which is shown in Fig. 1.

The photocurrent, photovoltage and power conversion efficiency characteristics for DSSCs were measured under illumination of simulated sunlight coming from a solar simulator with the radiant power of 100 mW/cm² (xenon lamp with AM-L5 filter). The incident light intensity was calibrated with standard si solar cell. The photocurrent densities versus photovoltage (J–V) characteristics were measured with dc voltage and current source which interfaced and controlled by computer. The short current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and overall power conversion efficiency (η) were determined from the J–V curve.



Fig. 2, FE-SEM images of photoelectrodes: (a) ZnO powder/CuO thin film, (b) ZnO powder/CuO powder, (c) ZnO powder/CuO nanowires and (d) ZnO powder, (e), (f), (g) and (h) showed cross-section Fe-SEM images of ZnO powder/CuO thin film, ZnO powder/CuO powder, ZnO powder/CuO nanowires and ZnO powder, respectively.

3. Result and discussion

3.1. Characteristics of photoelectrode

Fig. 2 showed FE-SEM images of photoelectrodes: (a) ZnO powder, CuO thin film, (b) ZnO powder/CuO powder, (c) ZnO powder/CuO nanowires and (d) ZnO powder. The ZnO/CuO thin film exhibited similar morphology as ZnO powder which had microparticle structure with diameter of about 200-500 nm. However, the morphology of ZnO powder/CuO powder showed microparticle structure with large diameter of about 1-3 µm while the morphology of ZnO powder/CuO nanowires showed wire-like nanostructure on microstructure with diameter of about 50-200 nm and length of about 10 µm. It should be noted that the color of the copper powder and thin film turned into black color after the heating process indicating the phase change to CuO. Fig. 2(e), (f), (g) and (h) showed cross-section FE-SEM images of ZnO powder/CuO thin film, ZnO powder/CuO powder, ZnO powder/ CuO nanowires and ZnO powder, respectively. The thickness of ZnO layer, CuO thin film, CuO nanowire and CuO powder obtained from cross-section FE-SEM images was about 20 µm, 1-3 µm, 10-20 µm, and 5-10 µm, respectively.

Fig. 3 showed XRD pattern of (a) ZnO, (b) ZnO/CuO powder, (c) ZnO/CuO nanowire, and (d) ZnO/CuO thin film on FTO glass substrates. For all cases, ZnO peaks and SnO₂ peaks from FTO were observed. It can be seen that CuO peaks were observed without copper peak for CuO layer cases indicating copper was completely oxidized to CuO.

3.2. Photoelectrochemical characteristics of ZnO DSSC

Fig. 4 showed J–V characteristic of ZnO DSSCs with ZnO/CuO layer as a photoelectrode. For comparison, J–V characteristic of ZnO DSSCs without CuO is also shown in Fig. 4 The photoelectrochemical parameters such as short current density, open circuit voltage, fill factor and the overall power conversion efficiency which determined from the measured J–V curves were summarized in Table 2.

Clearly, ZnO DSSC with CuO thin film as a barrier layer showed highest short current density of 5.10 mA/cm², and highest power conversion efficiency (η = 0.92%). This could be explained in terms of low back or reverse current due to the retardation of the interfacial recombination dynamics of CuO blocking layer [10].

Typically, a charge transfer processes of the Eosin-Y sensitized solar cell based on ZnO are illustrated in Fig. 5(a). When the Eosin-Y sensitizer absorbs a photon and transform to excited state, an electron



Fig. 3. This figure showed XRD pattern of (a) ZnO, (b) ZnO/CuO powder, (c) ZnO/CuO nanowire, and (d) ZnO/CuO thin film on FTO glass substrates.



Fig. 4. This figure showed J-V characteristic of ZnO DSSCs with ZnO/CuO layer as a photoelectrode.

filled in the lowest unoccupied molecular orbital (LUMO) of Eosin-Y and the electron injects to the conduction band of ZnO as in equation

$$D^* \rightarrow D^+ + e_{Z_{00}}$$
(1)

where D^* , and D^+ are excited dye, and oxidized dye, respectively. After that, injected electron diffuses through FTO and flow through the load via the external circuit and then reach the counter electrode. At counter electrode, the oxidized redox species (R^+) is subsequently reduced back to the *R* through accepting electron. R^+ is generated from the chemical equation

$$D^+ + R \rightarrow D + R^+$$
(2)

where D, R and R^+ is an original dye, redox species, and oxidized redox species, respectively. This equation is usually called dye regeneration process. The oxidized dye is quickly reduced back to its original state by reduce redox species (R) in the electrolyte for a complete cycle of electron transfer.

Moreover, the observed photocurrent density is given by

$$J_{\rm ph} = J_{\rm inj} - J_{\rm r} \tag{3}$$

where J_{inj} is the electron injection current resulting from dye sensitization and J_r is the surface recombination current which depends on back electron transfer. The back electron transfer which causes energy-wasting recombination has several possible pathways. Two important pathways are the recombination of e_{ZnO} with the oxidized dye before the dye can be generated and the recombination of e_{ZnO} with the oxidized redox species [17].

In our case, CuO layer was coated on top of ZnO photoelectrode to form a barrier layer. As shown in the energy level diagram in Fig. 5(b), conduction band (CB) of ZnO (-0.25 eV, NHE) [18] is situated below the CB of CuO (-0.8 eV vs. NHE.) [19]. Therefore, electron transfer from CuO to ZnO was thermodynamically permitted. Also, the potential difference derived from the difference of CB between CB of

Table 2

Summary of the photoelectrochemical parameters such as short current density (I_{sc}) , open circuit voltage (V_{oc}) , fill factor (FF) and the overall power conversion efficiency (n) which determined from the measured I–V curves.

Type of photoelectrode	$V_{\rm OC}(V)$	$J_{sc}(m\Lambda/cm^2)$	FF	Eff(%)
ZnO/CuO thin film	0.45	5.10	0.40	0.92
ZnO/CuO nanowire	0.52	1.49	0.59	0.46
ZnO/CuO powder	0.50	1.11	0.61	0.33
ZnO	0.43	1.40	0.62	0.43

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Fig. 5. Energy level diagram of (a) ZnO photoelectrode and (b) ZnO/CuO layer otoelectrode

ZnO and CB of CuO can prevent electrons to back or reverse transfer to dye and electrolyte resulting in low back or reverse current. Thus, energy-wasting recombination is less, electron injection process to ZnO is more efficient and finally, short current density is higher.

However, DSSCs with CuO powder and nanowire exhibited lower efficiency than that of CuO thin film and comparable to DSSCs without CuO layer. This is due to the thickness of CuO powder and nanowire which had a thicker layer of CuO resulting in a retardation of the interfacial recombination dynamics of CuO blocking layer is comparable to dye excited-state decay and CuO blocking layer has almost no effect on DSSC performance.

Normally, the maximum open circuit voltage of ZnO DSSC depends on the difference of the energy level between redox potential of electrolyte and Fermi-level of ZnO. Thus, the open circuit voltage of ZnO DSSCs is independent with morphology and dye adsorption surface area of ZnO. This is in agreement with our results that open circuit voltage of ZnO DSSC shows close value for all samples.

4. Conclusions

The ZnO DSSCs with different photoelectrodes were studied on the effect of CuO layer as a barrier layer toward power conversion characteristics. CuO powder, nanowire and thin film were used as a layer on the top of ZnO layer to form a blocking layer. It was found that ZnO DSSCs with CuO thin film exhibited the highest current density and the highest power conversion efficiency than those without CuO thin film. The enhancement of the power conversion efficiency can be explained in terms of the retardation of the interfacial recombination dynamics of CuO blocking layer. However, DSSCs with CuO powder and nanowire exhibited lower efficiency than that of CuO thin film and comparable to DSSCs without CuO layer. This is due to the thicker layer of CuO powder and nanowire resulting in a retardation of the interfacial recombination dynamics of CuO blocking layer which is comparable to dye excited-state decay and CuO blocking layer has almost no effect on DSSC performance.

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