Preparation and Characterization of Nanostructured CuO Thin Films using Sol-gel Dip Coating

S.S. Shariffudin, S.S. Khalid, N.M. Sahat, M.S.P. Sarah, H. Hashim
Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
sobihana@salam.uitm.edu.my

Abstract. Nanostructured CuO thin films were deposited onto quartz substrates by sol-gel dip coating technique. The precursor solution was prepared by dissolving copper acetate powder into isopropanol with molarity of 0.25M. Preheating and annealing temperature were fixed at 250°C and 600°C respectively. This study focused on various film thicknesses by varying the frequent number of deposited layers. The effect of thickness on electrical, surface morphology and optical properties of CuO thin film were studied. The surface morphology was examined using field emission scanning electron microscopy (FE-SEM), surface profiler for thickness measurement, optical properties of CuO thin film were characterized by using ultraviolet-visible spectroscopy (UV-VIS) for transmittance and absorbance, and the electrical property was examined by using two point probes method. The films were found to be denser at higher film thickness due to lesser porous observed on the surface. The thickness of these CuO thin films varied from 87.14 – 253.58 nm and the direct band gap energy was observed in between 1.9 to 2.35 eV. Lowest resistivity was found for sample with a thickness of 253.58 nm.

1. Introduction
Copper oxide is known to exist in two semiconducting phases, namely cupric oxide or copper (II) oxide (CuO); and cuprous oxide (Cu₂O) [1]. An intermediate compound between the previous two, a metastable copper oxide, (Cu₄O₃) has been also reported [2]. CuO, which has a band gap between 1.4 – 2.1eV [3], exhibits versatile range of applications [4]. CuO crystallizes in a monoclinic structure with the lattice parameters of a=4.684 Å, b=3.425 Å, c=5.129 Å, and β=99.28°. CuO thin film has transmittance of 20% in the visible spectrum and it could reach 90% for the high wavelength of the visible region with 2 to 2.5 refractive index value [5]. CuO thin films were reported as p-type conductivity due to copper vacancies in the structure [6].

CuO is a promising semiconductor for solar cell fabrication, such as a solar absorber [7] due to high solar absorbency and a low thermal emittance. In addition, this compound has been employed for the fabrication of glucose sensors [8], as anodes in lithium-ion batteries [9], gas sensor [10], and catalysts [11]. An important advantage of using CuO is that it is non-toxic and its constituents are available in abundance.

In preparation of CuO thin films, various techniques have been used such as spray pyrolysis, chemical vapor deposition, electro deposition, thermal oxidation, sputtering process and also sol-gel [12] and so forth. Among these techniques, the sol-gel technique has been utilized as a potentially useful technique for preparation of even nanoparticles CuO because this technique very simple and low cost technique, which requires no sophisticated specialized setup [13]. Other than that, dip coating represents an efficient route to coat large surfaces [14].
This study focused on preparation of CuO thin film by sol-gel dip coating technique by varying the number of layers deposited to examine the thin film thickness. The effect of various film thicknesses to physical, optical and electrical properties of CuO thin film was studied and discussed in this paper.

2. Experimental

Several steps were involved in the preparation of the CuO thin films such as preparation of solution and substrates, deposition process, preheating, annealing process and characterization. The steps are explained in details as below.

2.1 Quartz Substrate Preparation & Solution Preparation

Quartz substrate was immersed in the ultrasonic bath machine for 10 minutes using certain chemicals that was used to remove the contaminants. Firstly, quartz substrate was cleaned using acetone, followed by ethanol and lastly with DI water. Then, the quartz substrates were blown with argon gas to dry it.

The starting precursor, copper acetate powder was considered based on molar concentration of 0.25M and dissolved into (di) ethanolamine (DEA) and isopropanol (IPA). Then, (poly) ethylene glycol was added as a stabilizer. The solution was stirred on a hot plate stirrer for 10 minutes to dissolve all the ingredients. The final solution was dark blue and clear without any suspension of particles.

2.2 CuO Thin Film Deposition and Characterization

Quartz substrates were dipped into the solution with a constant withdrawal speed 2mm/s. This deposition process was repeated for one to five times to achieve various thicknesses of the thin films. The samples were named as S1 for 1 layer, S2 for two layers, S3 for three layers, S4 for four layers and S5 for five layer films. After the deposition process, the CuO thin film was dried in the furnace at 250°C for 10 minutes immediately. Lastly, the CuO thin film was annealed at 600°C for 60 minutes for purpose of recrystallization.

For the measurement of surface morphology, field emission scanning electron microscopy (FE-SEM; model: JEOL JSM-7600F) with accelerating voltage of 5 kV was used. The film thickness was measured using surface profiler (model: Veeco Dektak 750) while to observed transmittance and absorbance, ultraviolet-visible spectroscopy (UV-VIS; model: JASCO V-670) was used. Gold metal contact with a thickness of 60 nm was sputtered onto the surface of the films. For I-V characteristic, two point probes system (solar simulator; model: CEP 2000) was used.

3. Result and Discussion

3.1 Physical Properties

FE-SEM micrographs were taken to investigate the surface morphology of the CuO films and are embedded in Fig. 1. It is clearly seen that the surfaces of the films are free of cracks. A strong influence of the film thickness to the morphology of the CuO is clearly observed. The films morphologies showed a homogeneous distribution of grains on the substrates with high porosity at lower film thickness. It is also observed that the films became less porous with the increased of the film thickness; therefore the surface of the films became denser. Changes in the film thickness also affect to the CuO grain size, where the average grain size was found to increase with the thickness and is shown in Table 1.
The thickness of the CuO thin films was measured and presented in Table 1. It is observed that the thickness of the CuO thin films increased when withdrawal speed decreased. The highest thickness was achieved at sample S5 with a thickness of 253.58 nm.

Table 1: Thickness of CuO thin film at different withdrawal speed

| Samples | S1  | S2  | S3  | S4  | S5  |
|---------|-----|-----|-----|-----|-----|
| Grain size (nm)  | 25.5 | 26.7 | 26.5 | 38.6 | 40.5 |
| Thickness (nm)  | 87.14 | 95.22 | 105.06 | 209.29 | 253.58 |

3.2 Optical Transmittance and Absorbance

Transmittance of CuO thin film was observed by using UV-VIS spectrometer as shown in Fig. 2. Transmittances of the thin films were sensitive to the film thickness, where the highest average transmittance in the visible wavelength was shown by sample S1. The increase of film thickness induces the reduction of the transparent percentage from 64.7% to 25.1% in the visible range. This result was expected as more photons are adsorbed in a material when the thickness is increased. Besides, this might due to the the structures of crystalline grain became denser as the film thickness increased, which is already proven by the FE-SEM images. This makes the light more difficult to get through the surface of thin films. From this figure, all samples show sharp absorption edges in the visible region and these absorption edges slightly shifted to longer wavelengths (red shift) when the thickness of the films increased from 87.14 nm of S1 to 253.58 nm of S5.
The optical band gap can be measured by extrapolation technique. In order to determine the direct optical band gap, was using the Taucs relationship as follows [15]:

\[(\alpha hv) = A (hv - Eg)^2\]  

Where \(\alpha\) is the absorption coefficient, \(h\) is Planck’s constant, \(v\) is the photon frequency, and \(Eg\) is the optical band gap. An extrapolation of the linear region of a plot of the graph of \((\alpha hv)^2\) on the y-axis versus photon energy (hv) on the x-axis, gives the value of the optical band gap, \(Eg\) [15]. Optical band gap is calculated and showed in Fig. 3.

Fig. 3: Graph of optical band gap of CuO thin film for (a) S1 (b) S2, (c) S3, (d) S4, and (e) S5
From Fig. 3, the values of the optical band gap of CuO thin films were tabulated in Table 2. The direct optical band gap energy of CuO was reported in the range of 1.46 - 3.0 eV [3, 16], which shows that our findings are comparable with others. It is observed that the optical band gap decreased from 2.35 eV for sample S1 to 1.9 eV for sample S5. The decrease of band gap indicates the improvement of the films with the increased of the film thickness. The shifts of the optical band gap might due to the decreased of defects in the thin films as reported by Sengupta et. al. [17]. Besides, it is also reported that the optical band gap could decreased with the increased of the grain size [18].

| Samples | S1 | S2 | S3 | S4 | S5 |
|---------|----|----|----|----|----|
| Optical band gap (eV) | 2.35 | 2.15 | 2.1 | 1.9 | 1.9 |

### 3.3 Electrical Properties

The current–voltage ($I$–$V$) characteristics of CuO thin films are presented in Fig. 4a. The $I$–$V$ dependence is linear within the studied voltage range of -5 to 5V, proving that the gold contact is ohmic with the thin films. The $I$-$V$ characteristic of the CuO thin films were highly affected by the film thickness in the deposition process. The graph shows that the current increased with the film thickness.

![I-V characteristic of CuO thin film with different withdrawal speed](image1)

![Resistivity and Conductivity of CuO thin films](image2)

Resistivity and conductivity of the CuO thin films were calculated and showed in Fig.4b. Highest resistivity was 8.53 Ω.cm for sample S1 and decreased to 1.01 Ω.cm for sample S5. It was found that the values of resistivity decreased with the increased of the film thickness. This might due to the improvement of the optical band gap. Besides, with the increased of the grain size, the grain boundary would decrease, which subsequently would decrease the scattering of carriers at the grain boundaries [19]. Therefore it would improve the conductivity of the films hence decrease the value of the resistivity.

### 4. Conclusion

In summary, thin film of CuO was deposited using sol-gel method on quartz substrate with different thickness by varying the frequent withdrawal times using dip coating method. The optical, electrical
and physical properties of thin films measured by FE-SEM, UV-Vis spectrometer, surface profiler and two probe solar simulator. Film with lowest thickness showed the highest transmittance percentage. The decrease of the optical band gap with the increased of the thickness might attributed by the increased of the grain sizes. For $I-V$ characteristics, the best output current was shown by film S5 with thickness of 253.58 nm, which showed lowest resistivity value of 1.01 $\Omega \cdot cm$.

Acknowledgement
The authors would like to thank staff of NANO-Electronic Centre (NET) and NANO-Scitech Centre (NST), Universiti Teknologi MARA for the laboratory facilities. Also special thanks to Faculty of Electrical Engineering, Universiti Teknologi MARA for funding this project.

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