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# THE EFFECT OF SPIN COATING RATE ON MORPHOLOGY AND OPTICAL PROPERTIES OF CUPROUS OXIDE THIN FILM PREPARED BY SOL-GEL TECHNIQUE

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## ABSTRACT

Cuprous oxide thin films were successfully grown on indium tin oxide (ITO) coated glass by sol-gel spin coating using diethanolamine (DEA) as a solubility agent. The films were annealed at 350 °C in 5% $H_2$ + 95% $N_2$ atmosphere. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet-visible (UV-vis) spectroscopy. The effect of spinning rate on deposition on the microstructure, thickness and optical properties of cuprous oxide films was investigated. Based on the SEM micrographs of the as obtained films, we found that the grain size decreases with the increase in spinning rate. At the rate of 6000 rpm, the film shows better coverage with the rounded shape grain size is about 45 nm. Optical absorbance of the films was in the regions of 400-800 nm wavelengths. The optical band gap values of the films are in the range of 2.0-2.2 eV.

## INTRODUCTION

Cuprous oxide ($Cu_2O$) is a semiconductor which shows a varying optical behaviour because of stoichiometric deviations arising from its preparation methods and parameters [1]. It is a p-type direct-gap semiconductor due to the presence of Cu vacancies which form an acceptor level 0.4 eV above the valence band. The direct optical band gap energy values for $Cu_2O$ are between 2.1-2.6 eV [2]. Several authors have reported the potential use of the material in solid state photovoltaic cells because it is environmentally friendly and available abundantly. Moreover $Cu_2O$ semiconductors have the potential to fabricate at significantly lower cost as compared to silicon [2, 3]. $Cu_2O$ have been prepared by various methods, such as electrodeposition [4], wet chemical method [5], reactive magnetron sputtering [2], activated reactive evaporation [6] and sol-gel technique [7]. However, sol-gel technique has advantages over other methods due to simplicity in terms of process, relatively cheaper and produces materials of good homogeneity [7].

In this work, $Cu_2O$ thin films have been prepared using the sol-gel spin coating process. The as-prepared films were annealed at 350 °C in 5% $H_2$ + 95% $N_2$ in order to get single phase $Cu_2O$ films. The effect of spin coating rates on the morphology and optical properties of films is reported.

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## EXPERIMENTAL DETAILS

Copper(II) acetate, ($Cu(C_2H_3O_2)_2$, 99.999 % purity) was used as starting material for the synthesis of cuprous oxide thin films. The details preparation of cuprous oxide thin film was published previously [8].Using a spin coater, the solution was transformed into thin film form. Indium tin oxide (ITO) coated glass was used as substrates. The coating rates used was 2000, 4000 and 6000 rpm and the coating time was set to 40 s for all films. 40 s of coating is sufficient for having the solution spreading completely onto substrate. The as-coated films were dried at 250 ºC in air for 15 min to evaporate the solvent. The process was repeated to produce two layers of coating. Films were annealed at 350 °C for 1 h in 5% $H_2$ + 95% $N_2$ atmosphere. Annealing temperature 350 °C was found to be suitable for the formation of $Cu_2O$ phase in hydrogen atmosphere. Since the higher annealing temperature would produce Cu phase.

The microstructure of the films was studied using X-ray diffractometer (XRD) model D-5000 Siemens. The morphology of the film was observed using scanning electron microscope (SEM) model LEO VPSEM 1450 and optical properties were measured using ultraviolet-visible (UV-vis) spectroscopy model Perkin Elmer Lambda 900 in the range 300-850 nm. The chemical state of films was analyzed by X-ray photoelectron spectrometer (XPS) model Kratos XPS-XSAM HS.

## RESULTS AND DISCUSSION

*X-ray diffractometer (XRD)*
Figure 1 shows the grazing angle of X-ray diffractometer (GAXRD) patterns obtained for two layers of coating with 2000 rpm for 40 s followed by annealing at 350 °C in 5% $H_2$ + 95% $N_2$ atmosphere. The GAXRD pattern revealed a crystalline cubic $Cu_2O$ film characterized by two peaks, (111) and (200). The observed peaks matched the characteristic peaks of the mineral cuprite, $Cu_2O$, (JCPDS #. 01-075-1531).

*Scanning electron microscopy (SEM)*
Figure 2 shows the surface morphology of the $Cu_2O$ film grown onto ITO substrate. All films exhibit a smooth continuous film. The micrographs revealed that the films were in orderly form consisting fine grains of rounded shape. The average grain sizes obtained at various spinning rates were approximately 61 nm for 2000 rpm, 49 nm for 4000 rpm and 45 nm for 6000 rpm. The mechanism of spinning is after dropping the coating solution onto the substrate, the degree of coating is controlled by the centrifugal force derived from the rotation perpendicular to the substrate. At low rotation speed, the coating solution spreads out on the substrate, and at high rotation speed thin films are formed. The spin coating method, distinctively compared to the conventional physical and chemical method, is a quite simple and effective way of making thin films with varying its thickness by just controlling parameters such as the time and speed of rotation.

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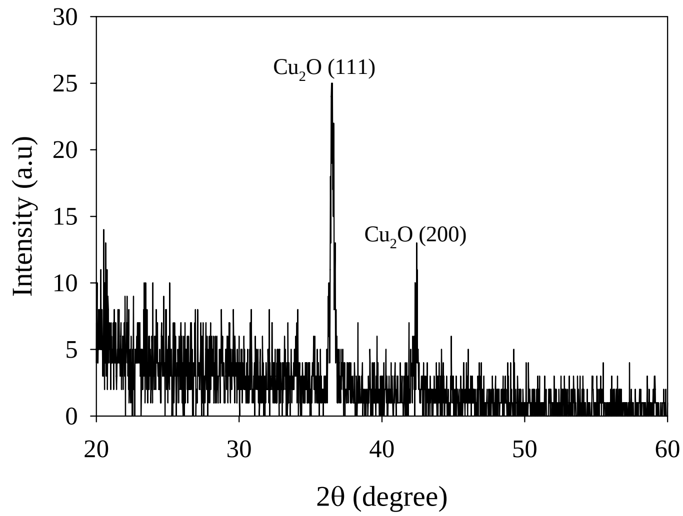


Figure 1: X-ray diffraction pattern of cuprous oxide film annealed at 350 ºC in 5% $H_2$ + 95% $N_2$ atmosphere.

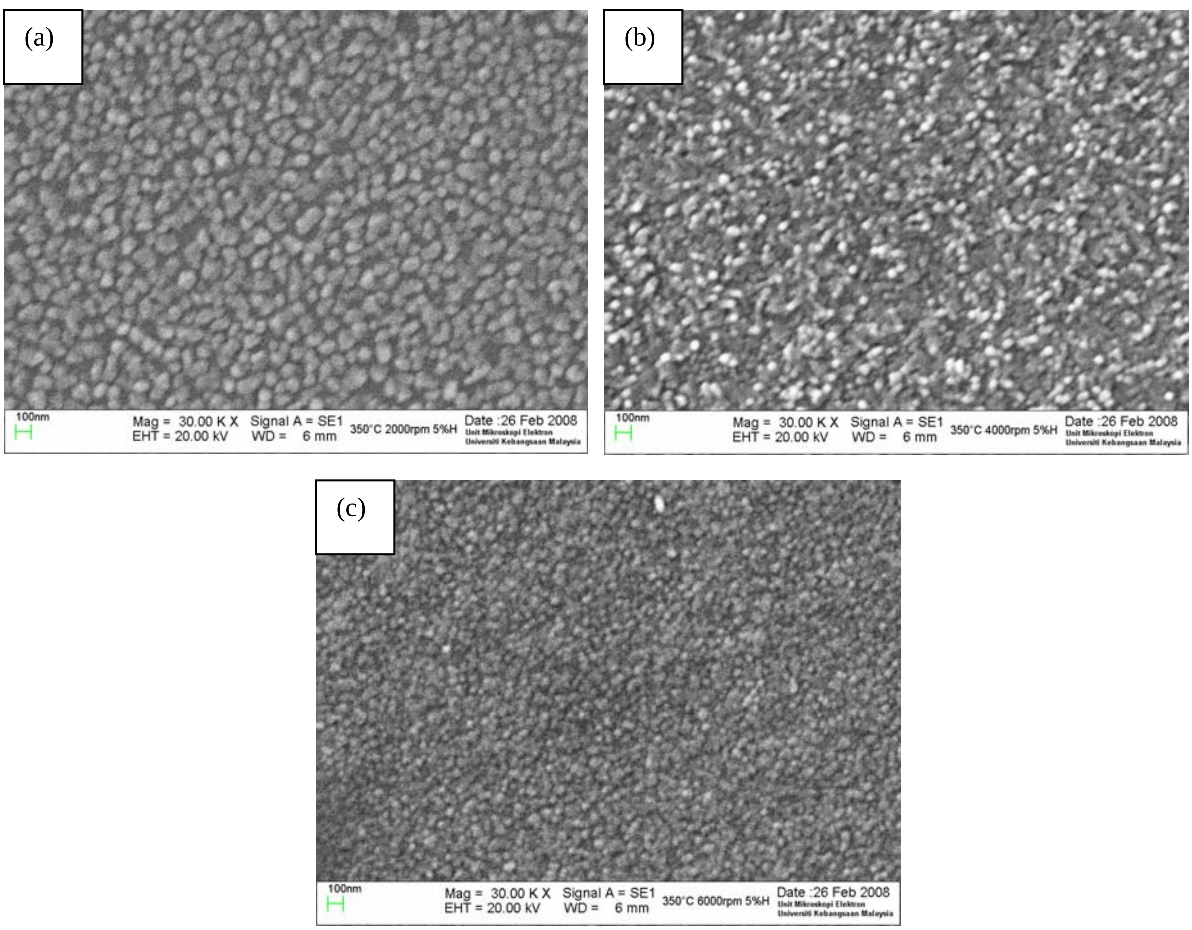


Figure 2. SEM micrographs of cuprous oxide films grown on ITO at different spinning rate (a) 2000 rpm, (b) 4000 rpm and (c) 6000 rpm

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The average thickness of the films measured using the scanning electron microscopy are 108 nm, 64 nm and 62 nm for spinning rates of 2000, 4000 and 6000 rpm, respectively. The lower the spinning rate, the thicker the film. The thicker $Cu_2O$ film, meaning that it would absorb more energy of sunlight and it is suitable for solar cell application [9]. In general, changing the spin rates does not influence the grain size significantly.

### *3.3 X-ray photoelectron spectrometer (XPS)*

Figure 3 shows the XPS survey scan of the film grown at 2000 rpm for 40 s. The survey scan shows the presence of copper, oxygen and a small adventitious carbon peaks. The spectra presented here have been charge corrected by using the C 1s peak (binding energy 284.5 eV). High energy resolution scans of the Cu 2p and O 1s peak are consistent with the presence of $Cu_2O$. The Cu $2p_{1/2}$ peak binding energy of 932.4eV shows excellent agreement with the value of 932.4-932.5 eV quoted in the literature [7,10]. Furthermore, $Cu_2O$ is characterized by a very small satellite, while CuO is characterized by a very large satellite peak which is not observed on these samples..

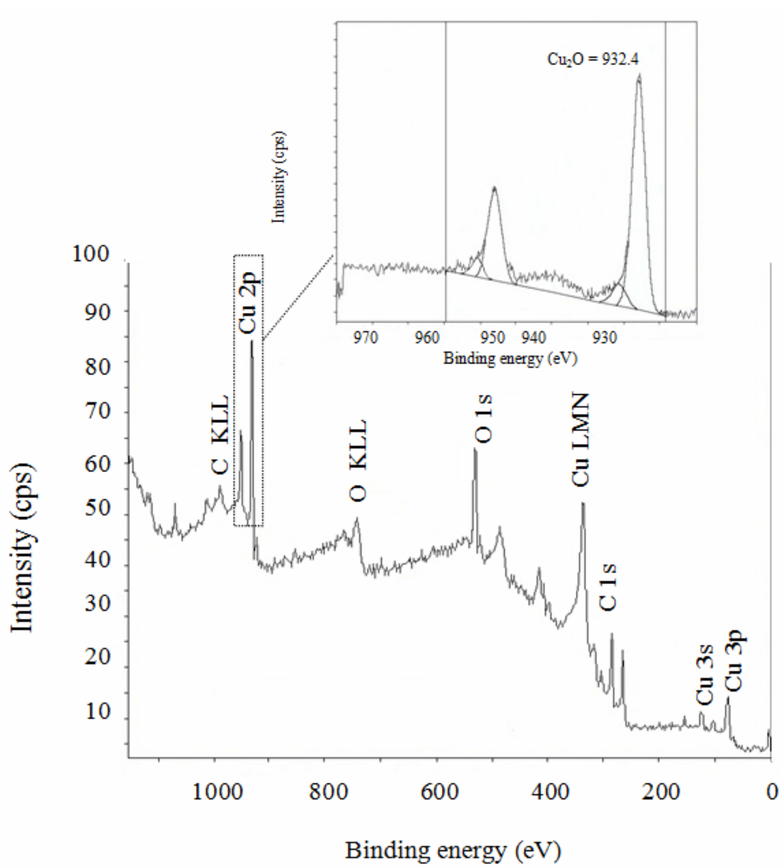


Figure 3. XPS survey scan of $Cu_2O$ thin films grown at 2000 rpm for 40 s and the inset is a high resolution scan of Cu 2p region

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The oxygen high resolution scan has two peaks at 530.7 eV and 531.7 eV. The peak at 530.7 eV shows a good agreement with the 530.4 eV reported for $Cu_2O$ [11]. The peak at 531.7 eV has previously been ascribed to absorbed water from the atmosphere. No other phases detected by XPS which is in good agreement with the GAXRD pattern

### *3.4 Ultraviolet-visible spectroscopy (UV-Vis)*

Figure 4 shows the optical absorbance spectra of $Cu_2O$ films on ITO coated glass grown at three different spinning rates followed by anneal at 350 °C. The absorbance of each film decreases with increasing of wavelength. The absorbance of the $Cu_2O$ film growing using 2000 rpm spinning rate is higher than that of the films grown at 4000 and 6000 rpm. It might be due to the different in thickness of the films. The lowest spin rate produced the thickest film with the highest absorbance, while the highest spin rate produced the thinnest film with the lowest absorbance. The absorption coefficient, $\alpha$ of the $Cu_2O$ film is related to the photon energy $hv$, [12].

$$(\alpha hv) = (hv - E_g)^{1/2} \quad (1)$$

where $hv$ is the photon energy and $E_g$ is the optical band gap. These band gaps are calculated from the intercept of straight line on the photon energy ($hv$) of the $(\alpha hv)^2$ vs ($hv$) plot and the values are listed in Table 1. The optical band gap for these films was found to be in the range of 2.0-2.2 eV and was found to be influence by film thickness. The high absorbance of $Cu_2O$ thin film at 2000 r.p.m over a wide wavelength range of 300-500 nm and the value of band gap 2.0-2.2 eV would make the film a potentially good material for photoelectrochemical solar cell.

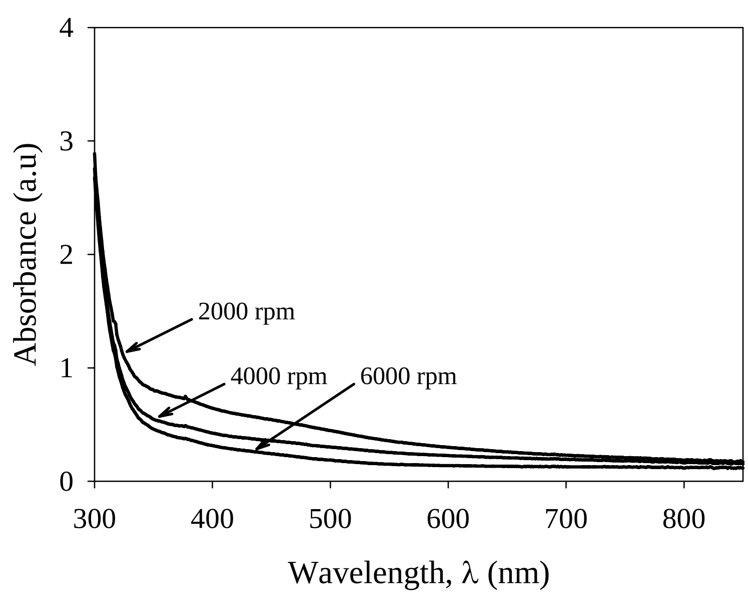


Figure 4. Optical absorbance against wavelength of cuprous oxide films prepared at 2000, 4000 and 6000 r.p.m and annealed at 350 ºC.

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The thickness, grain sizes and optical band gaps of the films grown at different spin rates are shown in Table 1. The optical band gap increased with spinning rate. The increasing in grain size of film with decreasing of spinning rate will also contribute to the reduction in optical transparency through optical scattering [13].

Table 1: The relationship between optical properties, spin rate and grain size of cuprous oxide films prepared by sol-gel technique.

| Spinning rate (r.p.m) | Grain size (nm) | Thickness (nm) | Optical band gap (eV) |
|---|---|---|---|
| 2000 | 61 | 108 | 2.08 |
| 4000 | 52 | 64 | 2.16 |
| 6000 | 45 | 58 | 2.20 |

## CONCLUSIONS

Cuprous oxide films have successfully been deposited on indium tin oxide (ITO) substrates by a sol-gel spin coating technique using copper(II) acetate. The films are single phase of $Cu_2O$ with cubic structure. The lower spin rate (2000 r.p.m) produce a thicker film compared to the film obtained at higher spin rate (6000 r.p.m). The thickest film (108 nm) with high absorbance is potentially suitable for a photoelectrochemical solar cell application.

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