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CHARACTERIZATION OF CUPROUS OXIDE THIN FILMS ON *n*-Si SUBSTRATE PREPARED BY SOL-GEL SPIN COATING

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ABSTRACT

Cuprous oxide films were successfully grown onto a *n*-Si substrate with (100) orientation via sol-gel spin-coating method at room temperature in air followed by annealing in 5% H_2 + 95% N_2 atmosphere. The annealed temperatures were varied between 350-550 ºC. The crystallinity and morphology of the oxide thin films were studied by grazing angle X-ray diffractometer (GAXRD) and scanning electron microscopy (SEM), respectively. GAXRD indicated that the crystallinity of the films increased with higher annealing temperature. SEM images revealed that the Cu_2O films form irregular grain size instead of smooth film which indicated the film growth followed Volmer-Weber growth mode. The size and shape of cuprous oxide grains also changed with temperature. Irregular shape with average size of 100 nm can be seen at annealed temperature 350 ºC which evolved into rectangular like shape with average size of 200 nm at annealed temperature 550 ºC. Optical reflectance revealed similar pattern for each film at wavelengths below 480 nm. It is believed that the absorption is due to energy gap of Cu_2O. The maximum reflectance for each film also varies which may be due to different coverage and size of the grains.

INTRODUCTION

Copper oxide thin films are semiconductor which is used as an active layer in various types of solar cells and a passive layer in solar selective surfaces [1]. Copper forms two well known oxides; cuprous oxide (Cu_2O) and tenorite (CuO) [2]. However, cuprous oxide is much sought due to its interesting properties.

Cuprous oxide (Cu_2O) is an interesting p-type semiconductor with a direct energy band gap of 2.0 eV. Cu_2O forms a cubic structure with a lattice parameter of 4.27 Å [3]. With these properties, Cu_2O leads to become a promising material in solar energy applications. Furthermore, it is cheap to produce and nontoxic with its component elements is readily available [4]. Due to its promising properties, various synthesizing techniques of Cu_2O have been reported. Among them are sputtering, thermal oxidation, vacuum evaporation, and sol-gel process [1-5]. Sol-gel technique however, remains among researchers favourite technique due to less equipment involve and cheap compare to most of the technique.

In this paper, Cu_2O is prepared using sol-gel technique because it is a soft bottom-up

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approach to achieve a good control over film composition and microstructure [5]. Particular attention was focused on the evolution of microstructure, crystallinity and the optical reflectivity of film as a function of annealing temperature and annealed under 5% H_2 + 95% N_2 atmosphere. There are no reports elsewhere in the effect of annealing under 5% H_2 + 95% N_2.

EXPERIMENTAL

The starting compound used in this study was copper (II) acetate in isopropyl alcohol and diethanolamine (DEA, $C_4H_{11}NO_2$) solution and mixed continuously. Small amount of glucopone was then added into the solution and continuously stirred for 24 hours using magnetic bar. The solution was then filtered using 0.45 μm filter prior to spin coating process.

Films were prepared by depositing the solution at room temperature by spin coating technique, onto an *n*-Si wafer with (100) orientation. The solution was spread onto the substrate at 3000 rpm for 40 s. The films were dried in the oven at 60 ºC for 10 min and the process was repeated to produce three layers of coating. The films were then annealed at various temperatures (350 – 550 ºC) for one hour in 5% H_2 + 95% N_2 atmosphere.

X-ray diffraction studies were carried out using a Bruker D8 Advance X-ray diffractometer (Cu $K_{\alpha 2}$, λ = 1.5406 Å). Scanning electron microscopy LEO 1450 VP was used to observe the surface morphology of films. Optical reflectance measurement was carried out using a UV-VIS Perkin Elmer Lambda 900 spectrophotometer.

RESULTS AND DISCUSSION

X-ray diffractometer

The GAXRD pattern (Figure. 1) reveals sharp peak diffraction for all of the prepared film, having more pronounced crystallinity at higher annealed temperature. The observed peaks matched the characteristic peaks of the mineral cuprite, Cu_2O, (JCPDs card no. 01-075-1531). Two characteristic peaks of Cu_2O at 2θ values of 36.462° and 42.419° corresponding to reflections from (111) and (200) planes single phase. The presence of other phases could not be detected by GAXRD indicating that only Cu_2O phase has formed. Si peak was not detected due to grazing angle of x-ray analysis; which x-ray can only penetrated about a few nanometers in depth. The diffracted beam has good peak to background ratios, which are relatively free from interference from the Si substrate [6].

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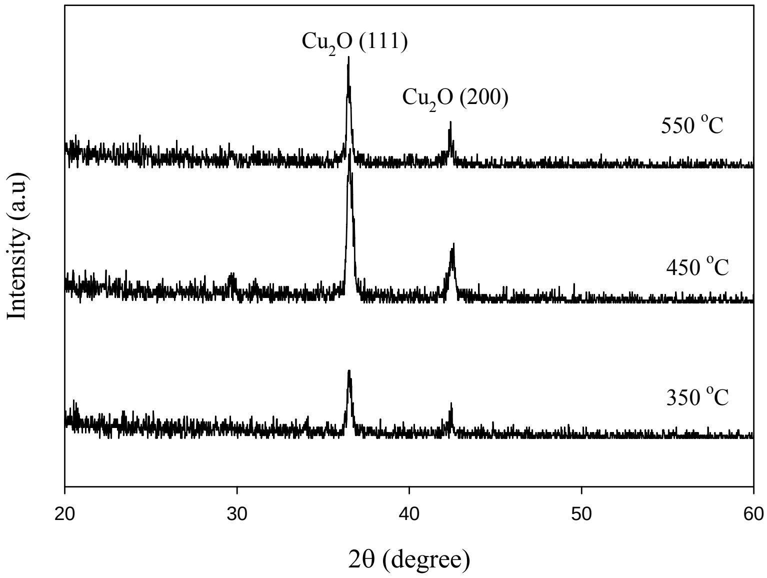

Figure 1: GAXRD pattern of Cu_2O thin films annealed at 350-550 °C in 5% H_2 + 95% N_2.

Scanning electron microscopy

Figure 2 shows the surface morphology of the Cu_2O film grown onto an *n*-Si substrate. All film exhibited 'island type' growth instead of smooth continuous film. The grain growths of Cu_2O observed most probably follow the Volmer-Weber growth, based on the shape and distribution of grain for each film. Furthermore, Volmer-Weber growth is most preferred growth mode typically for a normal metal film on semiconductor substrate [7]. It can been seen on the SEM micrograph that grain evolved from irregular shape with average size of 100 nm at 350 °C into a rectangular like shape with average size of 200 nm at 550 °C. The change of grain size is due to coalescence of each grain to form bigger grain with extra energy gain from the higher annealed temperature. This coalescence to form bigger grain is a typical phenomena since small grain tends to form a larger grain since larger grain are thermodynamically stabled. This phenomenon has been explained in depth by the Ostwald ripening mechanism [7]. Figure 2 (b) also shows that at 450 °C, the grain coverage is more conformal compared to sample annealed at 350 °C and 550 °C. This better coverage might explained the highest reflectance obtained (Figure 3) compared to other two samples. The nucleation and growth rate for sample 450 °C is seemed more uniform compare to 350 °C judging from the conformal coverage and size of grain. At 550 °C as been explained previously the small grain gaining energy would coalescence with each other to form larger grain as seen in Figure 2 (c).

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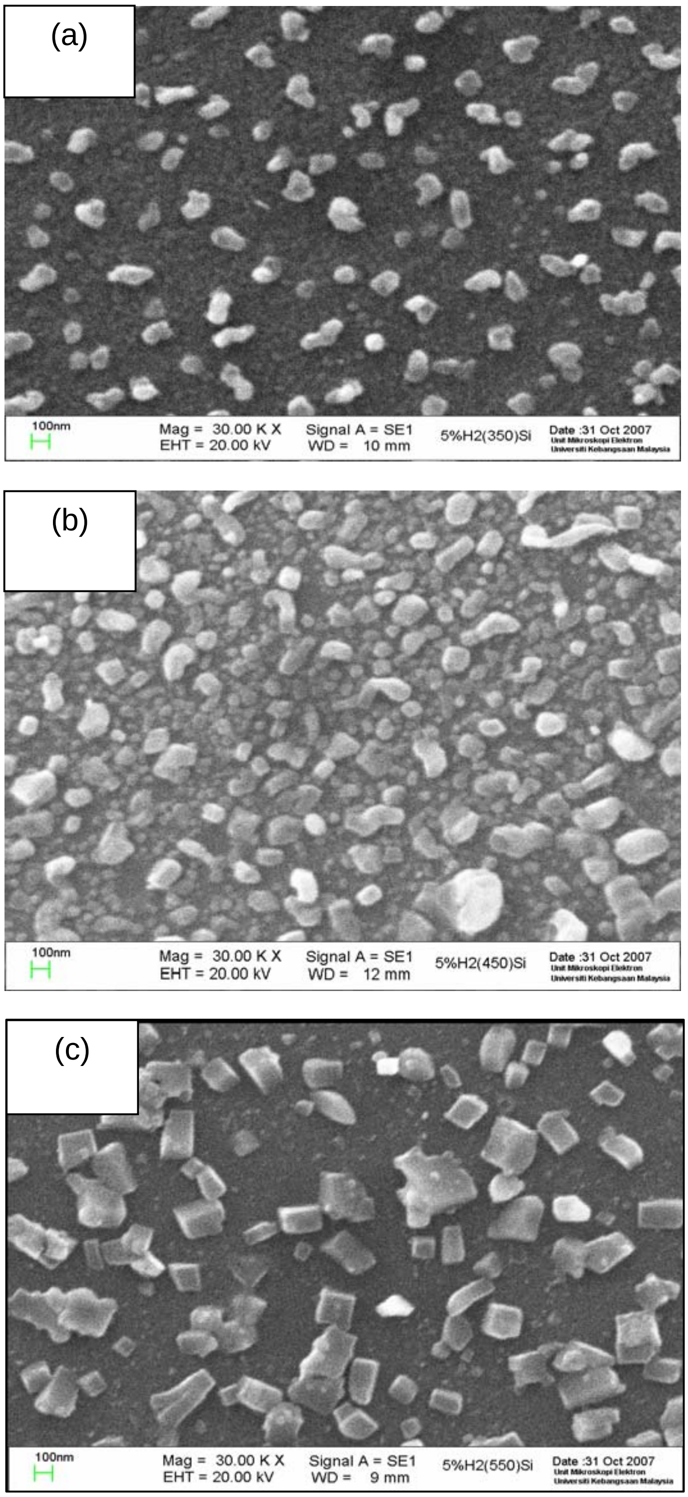

Figure 2: Scanning electron micrographs of thin films annealed (a) 350 °C, (b) 450 °C, (c) 550 °C

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Optical reflectivity
The optical reflectance spectra for each samples (Figure 3) shows a similar pattern where at below 480 nm the optical reflectance is low before increase to maximum at 650 nm. The variation of maximum reflectance is believed to be influenced by grain size, shape and coverage of samples. In case of films annealed at 450 °C, the better coverage (Figure 2b) is more conformal followed by 350 °C and 550 °C. The reduction of reflectance at below 480 nm for all samples may contribute to absorption by Cu_2O since the energy gap of cuprous oxide is reported at 2.0-2.2 eV [3]. This is the fact that no other phases are observed as in GAXRD and the substrate is Si which is indirect band gap and the energy gap is near 1120 nm region. There is a possibility of reduction of reflectance contribute by scattering at grain size as reported by [8]. However, light scattering happened for all range of wavelength not limited to certain wavelength. The drop of reflectance at below 480 nm most likely comes from absorption of Cu_2O energy excited from valence band into conduction band.

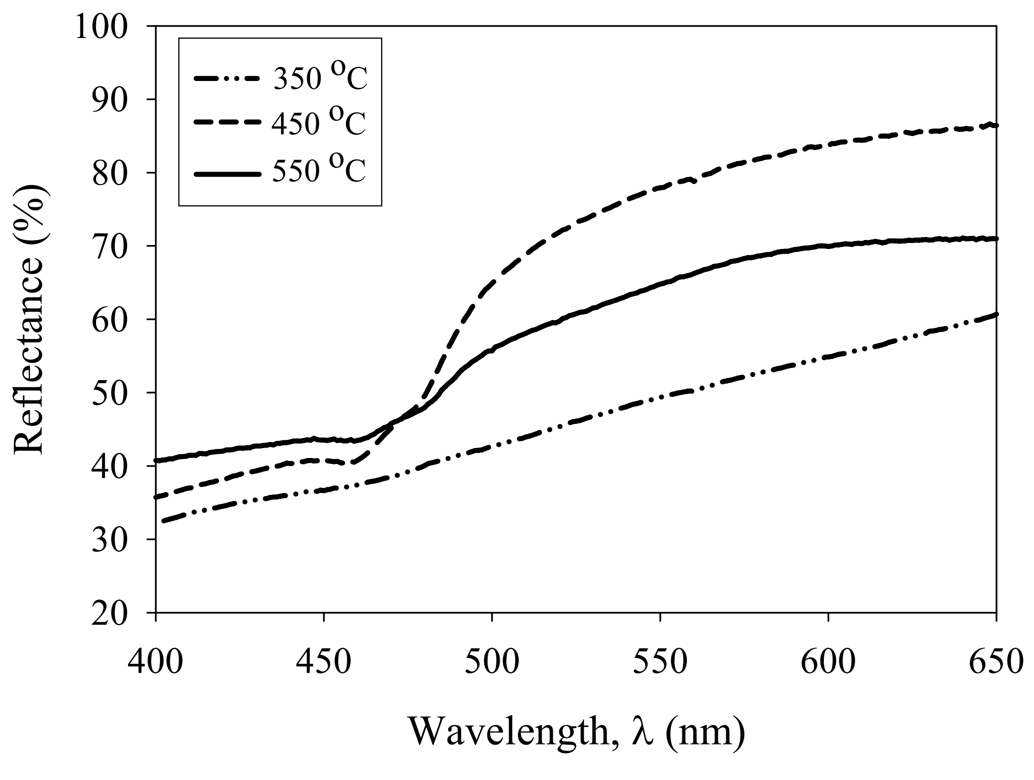

Figure 3: The optical reflectance (*R %*) as functions of wavelength (*λ*) under various annealing temperature

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CONCLUSIONS

The Cu_2O thin films were successfully grown onto *n*-Si wafer with (100) orientations by sol-gel spin coating and annealed at 350-550 °C. Single phase of Cu_2O thin films were produced at various annealing temperatures in 5% H_2 + 95% N_2 atmosphere. The evolution of microstructure and crystallinity of the films increased with annealing temperature. These results indicate that the annealing treatment can strongly affect the morphology and optical reflectance and absorption of film.

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