Investigation of Annealing Temperature on Copper Oxide Thin Films Using Sol-Gel Spin Coating Technique

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Abstract. Copper (II) Oxide or cupric oxide (CuO) is one of the well-known materials studied for thin films applications. This paper was studied on the effect of annealing temperature to CuO thin films using sol-gel method and spin coating technique. The solution was prepared by sol-gel method and the thin films were synthesized at various temperatures from 500ºC to 700ºC that deposited onto the quartz substrates. After the annealing process, the thin films were uniform and brownish black in colour. The measurements were performed by atomic force microscopy (AFM), surface profiler (SP), two-point probe and Ultraviolet-visible (UV-Vis-NIR) spectrometer. From the optical measurement, the band gap was estimated to be 1.44eV for sample annealed at 550ºC.

1. Introduction

CuO thin films are semiconductor material which normally used as an active layer in solar cells applications [1]. The investigation of the annealing temperatures on CuO thin films were usually deposited by many different methods such as dip coating, spin coating, chemical vapor deposition, electrochemical deposition, sputtering, and spray pyrolysis [5]. Spin coating technique was used in this paper fabricated with sol-gel method. There were many advantages by using sol-gel technique such as stable to decompose by sunlight, stable to heat, low temperature process and highly transparent [5]. Based on the research by Mohamammad Hossien Habibi et al [2] state that the copper oxide compounds could be used in the high temperature superconductors.

CuO thin films found to be a native p-type conductivity due to copper vacancies in the structure [11-14] with a band gap between 1.3eV and 2.1eV [3]. The optical absorption of CuO nanoparticles were controlled by the size and shape of nanostructure and the different in annealing temperature determined its activity [2]. Several samples of CuO thin films with temperatures range of 500ºC to 700ºC were reported in this paper. The research was to improve the microstructure of the CuO with annealing temperature.

The characterization of the CuO thin films were measured by I-V measurement, optical properties, surface morphology and thickness of thin films. The CuO thin films were characterized by its electrical and surface morphology using two-point probe technique and AFM respectively. Meanwhile, the thickness of the CuO thin films conducted by using SP. Lastly, the optical band gap energy was calculated by transmittance that conducted by UV-VIS NIR spectrometer.

2. Experimental Details
The procedures for preparing copper oxide thin films were summarized in this section.

2.1. Solution preparation
The quartz substrates with 2cm x 2cm dimension started with cleaning process. The five samples were immersed in acetone, methanol and distilled water sonicated with ultrasonic cleaner consecutively. Then, the solution was prepared by dissolving Monoethanolamine (MEA, C2H7NO) and Isopropanol in Copper Acetate Cu(CH3COO)2. H2O. Afterwards, (poly)ethylene glycol (PEG, H(OCH2CH2)nOH) was added to the prepared solution. Then it was mixed for 10 minutes using a magnetic bar and filtered on the hotplate with stirrer, Stuart (UC 152). The solution was prepared for 30 to 35 minutes long since no refluxing was required. Table 1 shows the ratio for chemical used in solution. Meanwhile, the powder of Copper Acetate was 0.25 gram. MEA was observed to be very effective and resulted in a very fast dissolution of copper acetate. The prepared solution with concentration of 0.25M was dark blue and clear. A double-step spinning program was applied to obtain homogeneous precursor films prior to heat treatment.

Table 1. The chemical ratio and quantity used in the CuO solution.

Chemical used	Ratio and quantity of chemicals	
	Percentage (%)	Mass (ml)
Isopropanol	5	4.5
Monoethanolamine (MEA, C_2H_7NO)	90	0.25
(poly)ethylene glycol PEG	5	0.25

2.2. Deposition of thin films
In first step, the solution was dropped in 10 times onto the substrates at 100 rpm for 10 seconds. The coating process of the thin films was used spin coater (WS-650-23B). Then, coating and drying of the precursor films were achieved during the second spinning step at 3000 rpm for 300 seconds on microscope quartz slides. Further drying and decomposition reactions occurred during pyrolysis in a chamber furnace, PROTHERM (PLF 160/25) at 250 ºC for five minutes following deposition each layer. After coating of the five layers which were the last layer of each sample, the films were annealed from 500ºC to 700ºC for 30 minutes.

2.3. The characterization of CuO thin films
The thicknesses of the thin films were measured using surface profiler (Dektak 150). Surface morphologies of the thin films were investigated using AFM. An UV-VIS-NIR Spectrophotometer (JASCO, FLH-740) was used to record the transmittance and absorbance between wavelength of 200nm and 1000nm. The PL spectra (CDRH Microscope Enclosure) were characterized in the wavelength range of 326nm to 900nm at room temperature. The current-voltage (I-V) measurement was conducted by using two point probes. Figure 1 shows the side view of the sample with Platinum as the metal contact for I-V measurement.
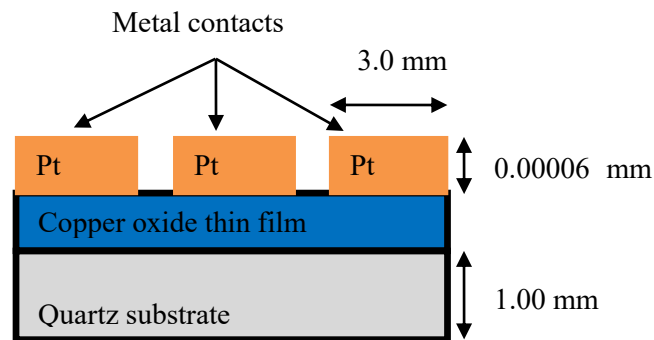
Figure 1. The side view of CuO thin film.

3. Results and Discussion
The results obtained from the experiment are discussed in this section.

3.1. Thickness measurement
Figure 2 shows the thickness of CuO thin films annealed at different temperatures. The graph shows that the thickness of CuO will increase as the temperatures getting higher. The thickness measurement was one of the parameter that could change the properties of the material due to surface phenomena [10]. The thickness of the nanocrystalline CuO thin films were measured using SP and found to be 70.7nm, 135.5nm, 173.2nm, 199.1nm and 255.3nm for 500ºC, 550ºC, 600ºC, 650ºC and 700ºC respectively.
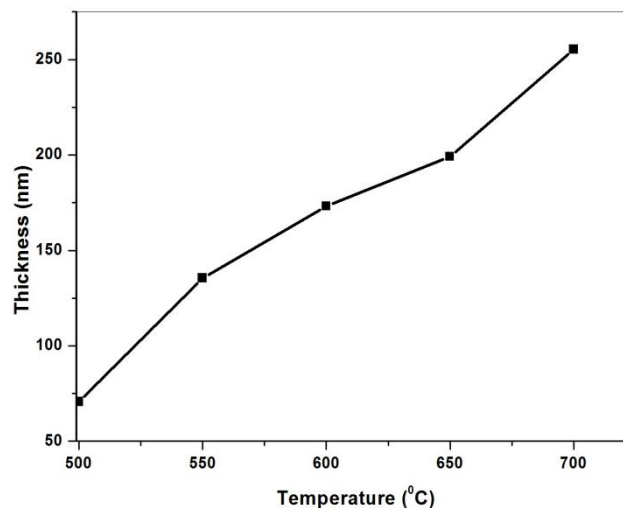

Figure 2. The thickness of CuO thin films at different annealing temperature.

3.2. Morphological Studies
AFM measurements were used to analyze surface morphology of the film films. Figure 3 shows the results of three dimensional (3D) AFM image of CuO film for different annealed temperatures. The surface evolution of the films showed "hills and valley" like structures, which are uniformly distributed over the entire substrate surface.
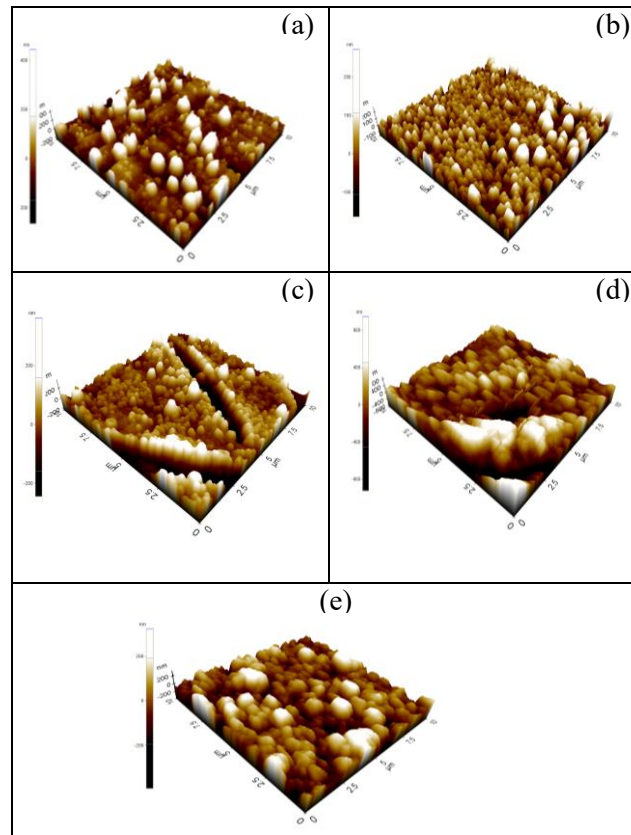
Figure 3. The AFM result of the CuO thin films at different temperature (a) 500ºC, (b) 550ºC, (c) 600ºC, (d) 650ºC and (e) 700ºC.

The grain size of CuO microstructures were getting bigger and harden with increasing of annealing temperature. Table 2 shows the mean value of thickness and surface roughness with the different temperatures. The thicknesses increases, same goes to the surface roughness also increases with increase in grain size. The sample A, B, C, D and E represent different temperatures of 500ºC, 550ºC, 600ºC, 650ºC and 700ºC respectively.

Table 2. The data of thickness and surface roughness.

Sample	Annealed temperature ($^{\circ}$C)	Thickness (nm)	Ra (nm)
A	500	70.7	42.63
B	550	135.5	52.27
C	600	173.2	60.43
D	650	199.1	67.34
E	700	255.3	76.52

Ripening of the grains causes growth from smaller to larger grain by surface diffusion which reduces the surface to volume ratio. Also higher substrate temperature stimulates elimination of grain boundaries and result in the formation of larger grains. These observations are in agreement with Chacko et al [12]. However, the results show that the thin films were uniform, dense, and well adhered to the quartz substrate.

3.3. Optical properties

Figure 4 shows the value of optical transmittance increases with higher the annealing temperatures. The CuO thin films prepared at a wavelength ranging from 300nm to 800nm, due to their reduced surface area.
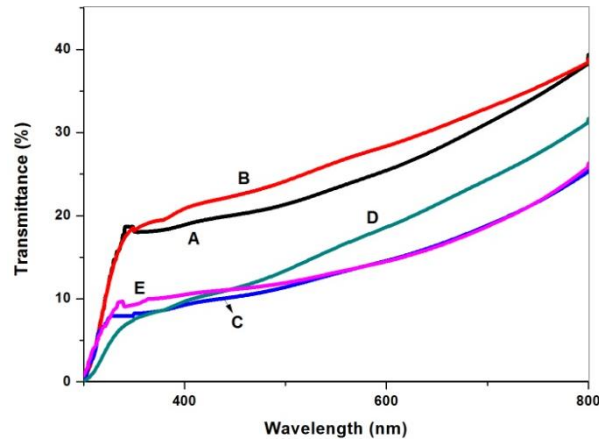

Figure 4. The transmittance of CuO thin films deposited at different annealed temperature (A) 500ºC, (B) 550ºC, (C) 600ºC, (D) 650ºC and (E) 700ºC.

Figure 5 illustrates the absorption coefficient (α) was calculated from the optical transmittance spectra by using UV-Vis Spectrometer. The absorption values were decreases in the visible region with increasing annealing temperatures. The results show that all samples have an abrupt absorption edge in the range of 400nm to 900nm. The results show the best plot temperature annealed at 500ºC and 550ºC. Meanwhile, the annealed temperature at 600ºC, 650ºC and 700ºC showed different trend from of the thickness. This showed the microstructures of CuO affect with the high temperature. From both Figure 4 and 5 show the optical transmittance increasing but the absorption coefficient decreasing with the higher annealing temperature.

As a direct band gap semiconductor, the relationship between absorption coefficient of the CuO thin films and incident phonon energy (hν) can be express as follow Equation 1 [5]:

$$hv = \frac{hc}{\lambda} \tag{1}$$

where h represent the Plank constant which was 6.63×10^{-34}, c was the light constant 3×10^{8} and λ was the wavelength. Meanwhile the absorption coefficient, α was calculated by using Lambert`s law as shown by Equation 2 below:

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \tag{2}$$

where t was the thickness of thin film and T was the transmittance values of the thin films. The Urbach energy is a parameter used to describe the band tailing phenomenon which normally defects in the thin films [10].
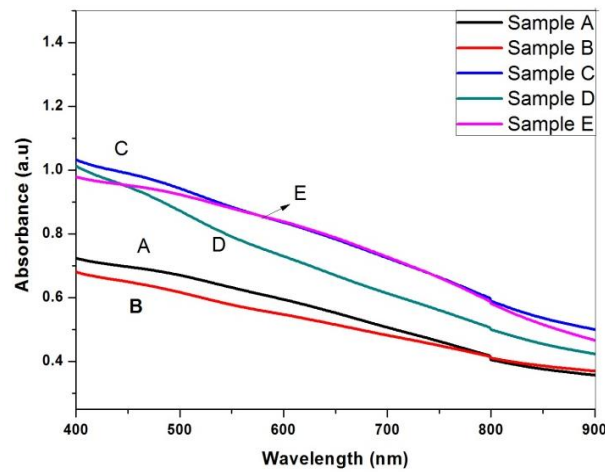
Figure 5. The absorbance deposited of CuO thin films measured by UV-Vis NIR Spectrometer at different temperature..

Figure 6 shows the reciprocal gradient of the plot in Figure 5 with the value of Urbach energy or optical energy band gap. From the plots, the optical band gap energy value of as deposited samples annealed at 500°C, 550°C, 600°C, 650°C and 700°C are 1.39eV, 1.44eV, 1.70eV, 1.85eVand 1.90eV respectively.
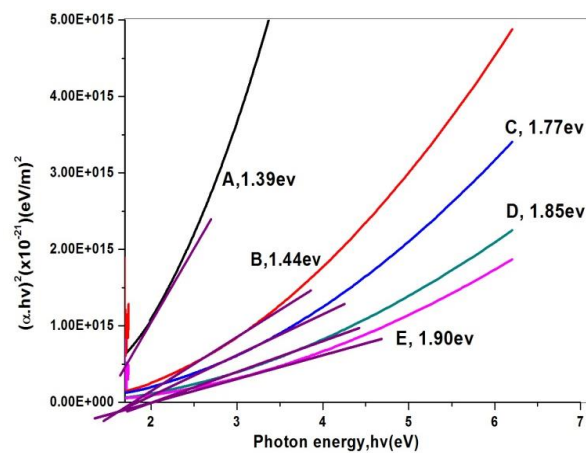

Figure 6. The plot of the (αhν) versus hν for CuO thin films.

The results show the optical energy band gap increases with annealing temperatures. The band tail widening from the plot shows that the defect of Cu (CH3COO)2. H2O doped CuO thin films increase with annealing temperatures. Based on the past research, this phenomenon could be from the broadening of donor levels into impurity band which merge with conduction band in the forbidden gap [5]. More Cu+ could be incorporated in CuO lattice structure by higher thermal energy obtained at higher annealing temperature due the increment of carrier concentration.

3.4. Electrical properties

I-V measurement plots of CuO thin films at different annealing temperature are shown in Figure 7. Platinum (Pt) was used as metal contacts during the measurement. The result indicates the Ohmic behavior of thin films with linear I-V curve observed for all annealed thin films. It also could be observed that the current value at fixed voltage increase with annealing temperatures to indicate the enhancement of electrons conductivity as annealing temperatures were increased. From the I-V curve, the resistivity, ρ of CuO thin films were calculated using following Equation 3:

$$\rho = \left(\frac{V}{I}\right)\frac{wt}{l} \qquad (3)$$

where ρ was the resistivity, V was supplied voltage, I was measured current, t was the film's thickness, w was the electrode width and l was the length between electrodes.
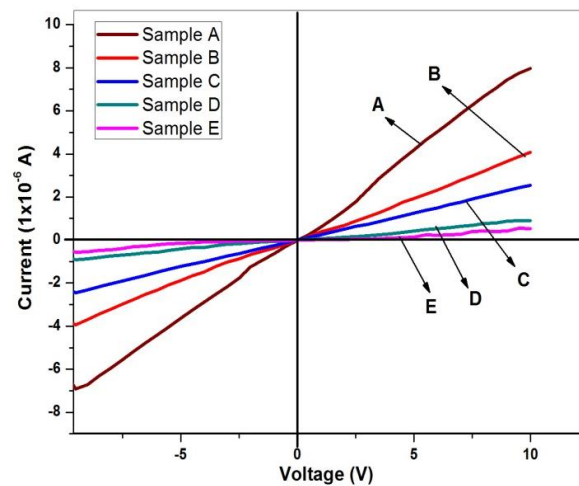

Figure 7. The I-V curve of CuO thin films at different annealing temperature.

The calculated resistivity obtained in this worked to be 2.27kΩm, 5.56kΩm, 7.86kΩm, 14.4kΩm and 38.3kΩm for thin films annealed at 500ºC, 550ºC, 600ºC, 650ºC and 700ºC respectively. The plot of CuO thin films resistivity with annealing temperature was shown in Figure 8. The temperature at 700ºC has the highest resistivity while the temperature at 500ºC has the lowest resistivity. It could be concluded that the resistivity of the CuO thin films are increase with increase of annealing temperatures.
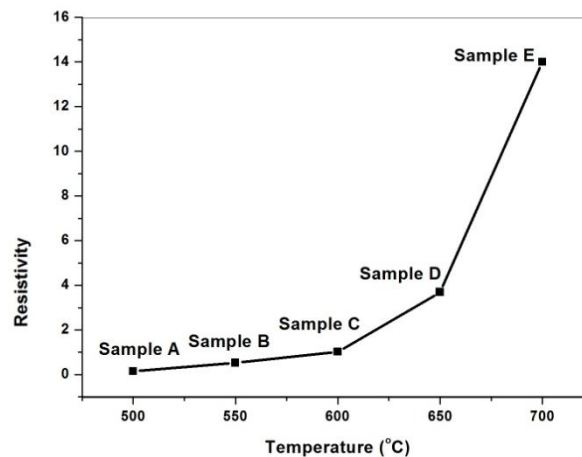
Figure 8. The resistivity of CuO thin films as an increasing of annealing temperatures.

The decreased in electrical conductivity at higher annealing temperatures could be due to the crystallinity with annealing temperature [5]. Dandeneau et al. [15] shows that the increment of carrier concentration by the ionization of oxygen vacancies with annealing temperature also contributed to the increment of electrical conductivity at higher annealing temperature.

4. Conclusion

The thin films were annealed at 500ºC until 700ºC. The thicknesses were increased by increasing temperature. The AFM revealed that the CuO thin film has a good surface morphology. All the thin films exhibit high transparency in the visible region with average transmittance above 16%. The energy optical band gap of CuO thin films increased as annealing temperature getting higher such as 1.44eV for sample annealed at 550ºC. It was proved by current-voltage (I-V) measurement indicates conductivity of CuO thin films has the highest plot at 500ºC and decreasing with the increasing annealing temperatures.

Acknowledgments

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