The Characterization of Copper Oxide with Different Molar Concentration Using Sol-Gel Spin Coating Method

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Abstract - **In this paper, the Copper oxide (CuO) thin films were deposited on 500um quartz substrates. The objective of this research was to study the effect of different molar concentration of the CuO thin films deposited using spin-coating technique. The molar concentration of CuO solutions used were 0.3M, 0.35M, 0.4M, 0.45M and 0.5M that prepared using sol-del method. These solutions were formed by dissolving copper acetate in isopropanol, diethanolamine and polyethyleneglycol. All samples were annealed at 600°C for 1 hour in a furnace. The electrical properties were measured to check their resistivity by two point probe technique. The electrical measurements showed that current increase when the concentration increase. The thicknesses were performed using the surface profiler while the surfaces morphology were characterized using Field Emission Scanning Electron Microscopy (FESEM). The films surfaces were smooth and uniformly distributed grains. The optical transmittances were measured using UV-Vis spectrometer and they decrease as their concentration increase.**

Keywords - Copper oxide; Concentration; Sol gel method; Spin coating technique.

I. INTRODUCTION

In the past decades, CuO thin films widely used in many technological fields to investigate their potential applications such as solar cell fabrication[1], semiconducting sensor [2, 3], electrochemical devices [4] and photovoltaic material [5]. CuO is I-IV compound semiconductor in periodic table and it is important because of high in optical absorption [6, 7], high electrical conductivity [8], non toxic environment [9] and less cost production. CuO is a p-type semiconductor with band gaps between 1.21 and 2.1eV.

Recently, many methods were reported to fabricate the CuO thin films. CuO thin films were prepared using several deposition techniques including chemical vapor deposition [10], RF magnetron sputtering [11], spray-pyrolysis [12], vacuum evaporation [3], electro-deposition [10] and etc. In this research, sol-gel method was used as technique to fabricate CuO thin film. The spin-coating method was chosen to fabricate CuO thin film because of it easily to use and inexpensive [7].

The main objective of this research was to study the effect of different molar concentration using sol-gel spin-coating method. The CuO thin films were deposited by spin-coating technique on the quartz substrates and annealed at 600°C in a furnace. The prepared thin films were characterized by using different techniques to investigate the effects of surface morphology, thickness, optical and electrical properties.

II. EXPERIMENTAL METHODS

There were several steps in this experiment which were the preparation of substrates and solution, deposition process, drying process, annealing process and characterization. The processes are summarized in the flow chart shown in Figure 1.

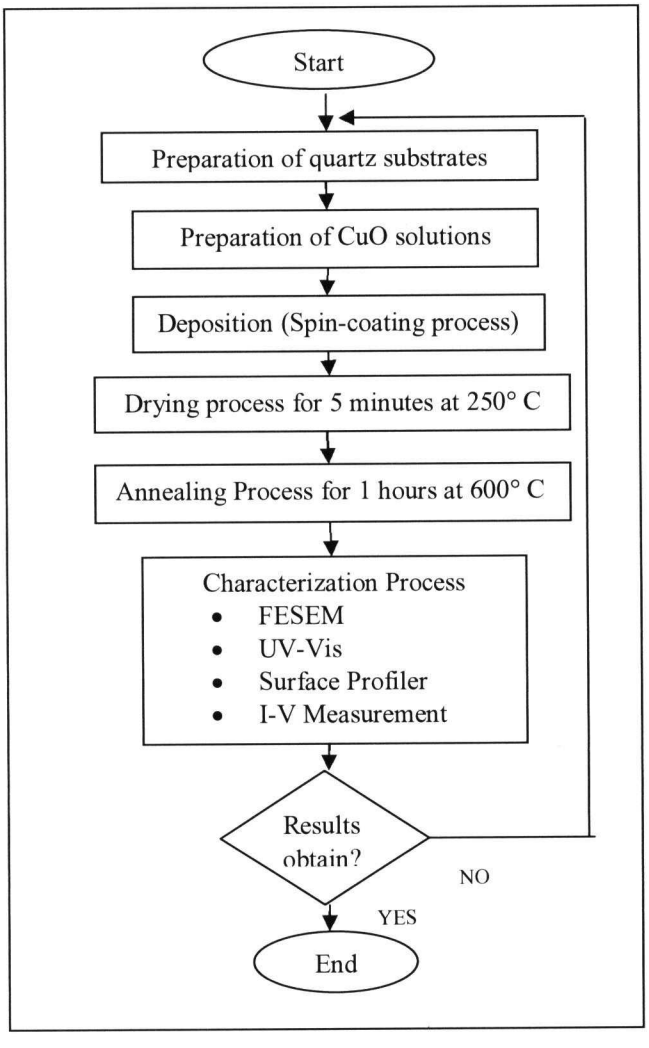

Figure 1: The flow chart of the experiment.

The CuO thin films were grown using a sol-gel method with spin-coating technique for different concentrations.

A. *Substrates Preparation*

The quartz substrates were cleaned in ultrasonic machine by using acetone, methanol and DI water for 10 min in sequence to remove the contamination. After that, quartz substrates were sprayed using nitrogen gas before deposition process.

B. *Preparation of CuO solution*

The CuO thin films were synthesized using a sol gel method. The copper acetate was used as a precursor. The quantities of the solutions were calculated by different molarities using Equation 1 below.

$$\text{Molarity} = \frac{\text{Moles of solution (mol)}}{\text{Total solution (ml)}} \qquad (1)$$

Table 1 shows the quantity of copper acetate powder used for the CuO solution.

TABLE 1. The quantity of copper acetate used for the CuO solution.

Sample	Molarity (M)	Quantity of Cu acetate (g)
A	0.30	0.299
B	0.35	0.349
C	0.40	0.399
D	0.45	0.449
E	0.50	0.499

CuO solutions were prepared by using copper acetate Cu(CH3COO).H2O, (poly) ethylene glycol (PEG, $H(OCH_2CH_2)_nOH$) and (di) ethanolamine (DEA, $C_4H_{11}NO_2$) . The copper acetate was dissolved in isopropanol and (di) ethanolamine[3]. Then, (poly) ethylene glycol was added to the resulting solution. The solutions were formed the dark blue and clear solution. Afterwards, the solutions were stirred at 700rpm with magnetic bar for ten minutes at room temperature using a magnetic stirrer. The quantity of chemical was used to prepare 5ml of solutions shows in Table 2.

TABLE 2. The quantity of chemical used for the CuO solution.

Solution	Quantity (ml)
Isopropanol	4.50
Diethanolamine	0.25
Polyethylene glycol	0.25

C. *Deposition Process*

The CuO thin films were deposited by spinning the quartz substrates on spin coater with dropping the solution. A double step spinning program was applied into the spin coater. First, the CuO solution was dropped onto the substrate with ten drops of the solution at 100rpm for 10 seconds. Then, coating of the films was achieved during the second spinning step at 3000 rpm for 300 seconds [3].

D. *Drying and Annealing processes*

After the deposition process, the CuO thin films were dried immediately for 5 minutes at 250°C in a furnace. This process was repeated for five times to get five layers for each sample. Lastly, after the coating of the last layer, the thin films were annealed for 1 hour at 600°C in a furnace [3].

E. *Samples Characterization*

Samples in different molar concentration were characterized for several properties. Field Emission Scanning Electron Microscopy (FESEM) was used to observe the surface morphology of the CuO thin films and their thicknesses were observed by using the surface profiler [2, 3]. Besides that, the absorbance and transmittance of CuO thin films were observed using UV-Vis spectrometer [13]. Measurement of I-V characteristics were performed by using two point probe method after CuO thin films were deposited by gold as the metal contact. The thickness of metal contact deposited onto the CuO thin film was 6×10^{-6} cm (60nm) while their width was 0.3cm. Figure 2 shows the cross section of CuO thin films.

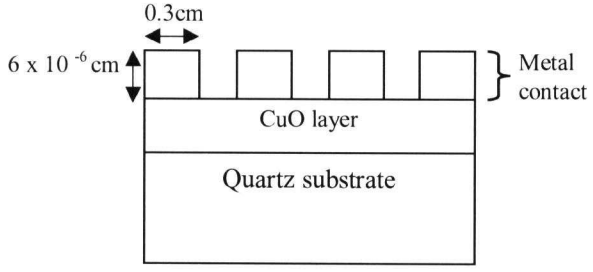

Figure 2: The cross section of CuO thin films.

III. RESULTS AND DISSCUSSIONS.

The results of CuO thin films of different concentration along with thickness, surfaces morphology, optical properties and I-V characteristic have been reported.

A. Thickness

The thin films thicknesses were estimated using Surface Profiler equipment. Table 3 shows the thicknesses of each sample that were deposited by different molar concentration of CuO.

TABLE 3. The thickness of CuO thin film at different molar concentration.

Sample	Molarity (M)	Thickness (nm)
A	0.30	302.38
B	0.35	349.78
C	0.40	358.56
D	0.45	517.86
E	0.50	662.33

Figure 3 shows the plot of thickness against number of different molar concentration. The graph shows the thickness increase from 302.38nm to 662.33nm with an increasing in molar concentration. It shows the higher molar concentration with higher thickness. The films thickness increased caused by increase of precursor viscosity and solubility [7].

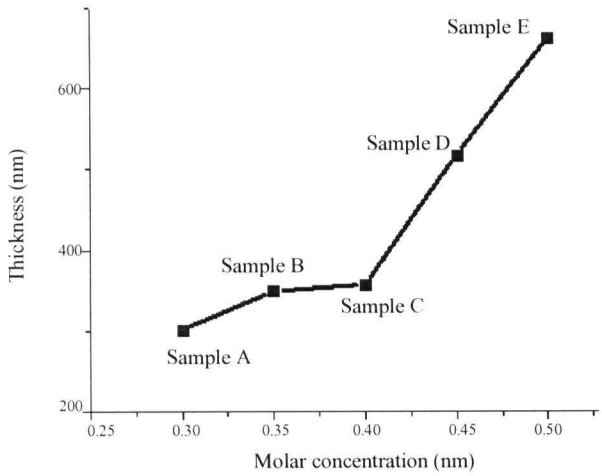

Figure 3: The plot of thickness vs. molar concentration.

B. Surface Morphology

The surface property of the films used to analyze surface morphology of a films and to determine the grain size. FESEM were taken to investigate the surface morphologies of the CuO thin films. Figure 4 represents FESEM images of the surfaces morphologies for five different molar concentrations (0.3M, 0.35M, 0.4M, 0.45M and 0.5M) labeled as a, b, c, d and e.

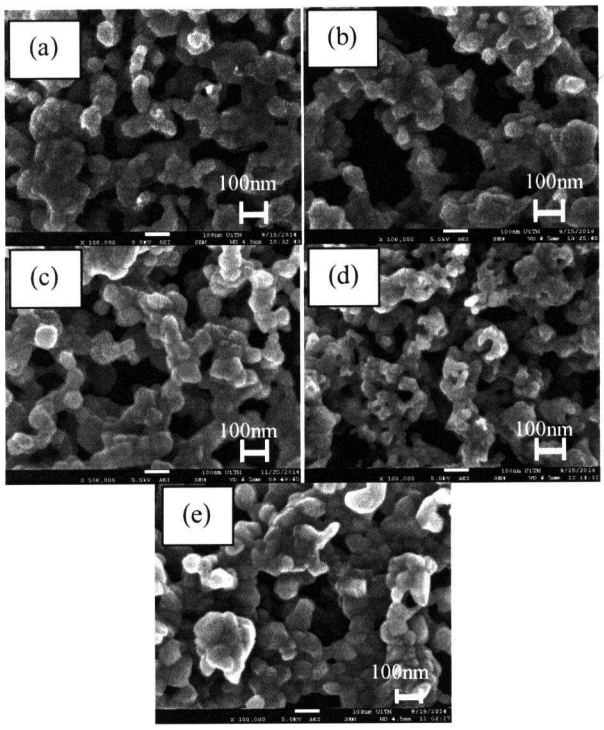

Figure 4: The FESEM images of CuO samples of (a)0.3M, (b)0.35M, (c)0.4M, (d)0.45M and (e)0.5M.

The deposited films were found to be smooth and good in distributed grains. From the surface of the thin films it were seen that there were no cracks which showed that the films are well adherent on the substrates. The average grain sizes are shown in Table 4.

TABLE 4. The average grain sizes of CuO thin film at different molar concentrations.

Sample	Molarity (M)	Average grain size (nm)
A	0.30	69.30
B	0.35	60.36
C	0.40	73.70
D	0.45	60.74
E	0.50	67.34

C. Optical Properties

The optical transmittance of the spin-coated CuO thin films in the spectral range from 200nm to 1500nm were obtained using UV-vis spectrometer as shown in Figure 5. It can be seen that the transmittances of CuO thin films were sensitive to molar concentration. The transmittances of CuO thin films decrease as their thickness increase with increase of molar concentrations. It starts to rise at wavelength 450nm.

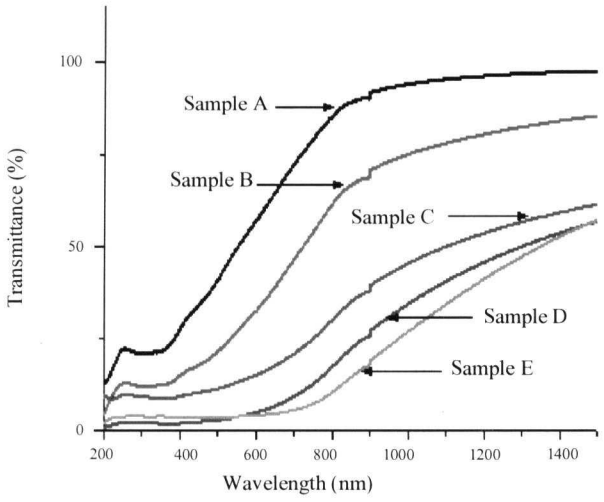

Figure 45: The plot of transmittance vs. wavelength.

The plots of absorbance are shown in Figure 6 where the results obtained were opposed with the transmittance.

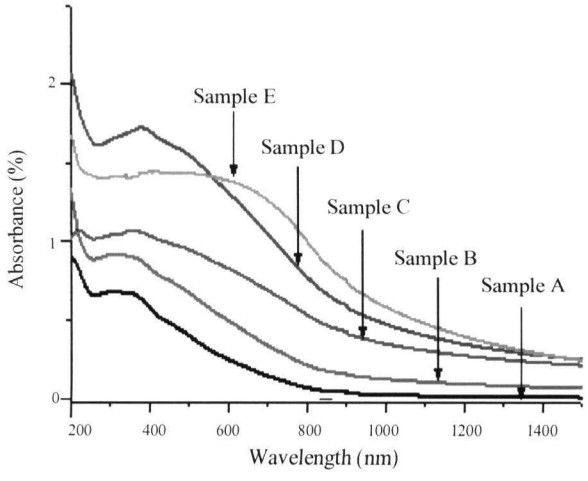

Figure 6: The plot of absorbance vs. wavelength.

The optical band gap for CuO thin films were shown below in Figure 7. These optical band gaps were measured by extrapolating technique. Extrapolation of the plots to the x-axis gives the band gap energy of the CuO thin films. The extrapolating technique is when plot were made between optical band gap and photon energy a linear graph shown in the Figure 7, which clearly suggested the direct nature of band gap in CuO thin films.

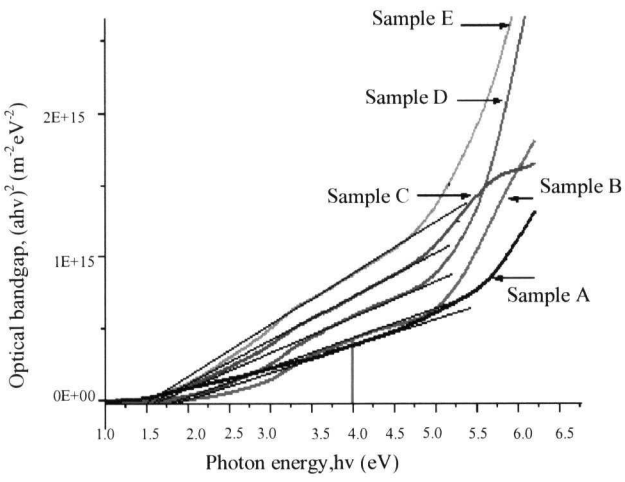

Figure 7: The plot of the optical band gap of CuO thin films.

The intercept on x-axis corresponding to photon energy determined the band gap values of the deposited CuO thin films. Figure 8 shows the focusing images of the optical band gap of CuO thin films.

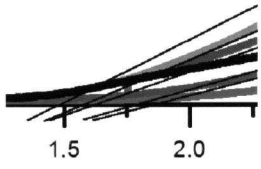

Figure 8: The subset plot of the optical band gap of CuO thin films between 1.0 until 2.0eV.

The energy band gap of CuO thin films for all samples are shown in Table 3 below.

TABLE 3. The energy band gap of CuO thin film at different molar concentration.

Sample	Molarity (M)	Band gap (eV)
A	0.30	1.90
B	0.35	1.81
C	0.40	1.63
D	0.45	1.59
E	0.50	1.51

The energy band gap shows between 1.9eV to 1.51eV for different molar concentrations. Higher deposited conditions of energy band gap are 1.9 eV were observed.

D. I-V Characteristics

I-V characteristics for all the samples are strongly dependent on the molar concentration in the deposition process. Figure 9 shows linear graph of the I-V measurement for all samples of different number of molar concentration. The subset plot shows the focusing images on the data between 0 until 2.5 V.

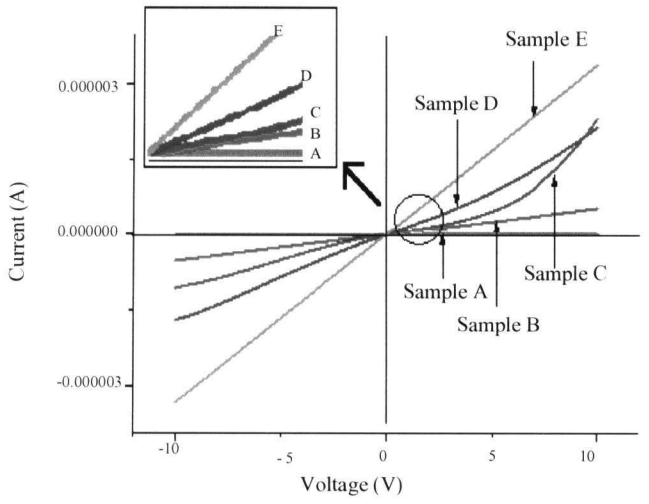

Figure 9: I-V Characteristics of CuO thin films with different molar concentration. The subset plot shows the range between 0V until 2.5V.

It shows the current increase when the molar concentration increase which follow Ohm's law which the current is directly proportional to the voltage as in Equation (2):

$$V=IR \qquad (2)$$

where, V is the voltage, I is the current and R is the resistance.

Figure 10 shows the resistivity decrease drastically when the molar concentration increases. The graph shows that the minimum resistivity is about 12.76Ω/m at molar concentration of 0.5M.

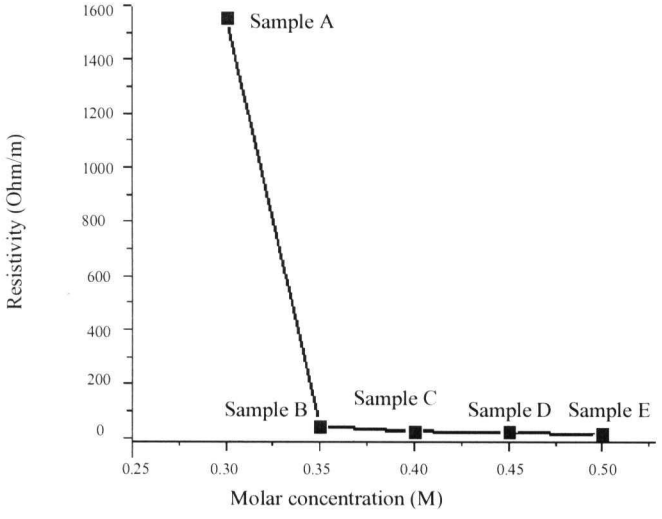

Figure 10: The plot of the resistivity of CuO thin films.

It can be prove by the calculation in Equation 3:

$$\rho = \left(\frac{v}{i}\right)\left(\frac{wt}{l}\right) \qquad (3)$$

where, ρ is the resistivity of the thin film, v is the voltage, i is the current, w is the width of metal contact, t is the thickness of the thin film and l is the length between the metal contact.

As shown in Figure 11, the molar concentration of 0.5M shows a maximum value of electrical conductivity is about 0.07 S/m. The conductivity was performed inversely from the calculated value of resistivity. The higher molar concentration shows the higher conductivity. It means that the ability of CuO thin films to conduct electric current is very high at 0.5M of molar concentration.

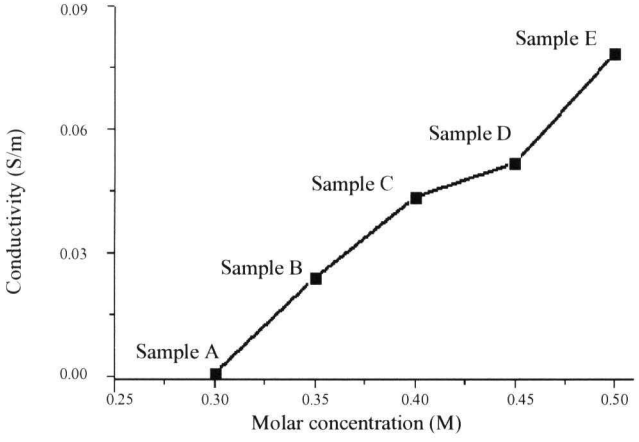

Figure 11: The plot of conductivity of CuO thin films.

This can be proved by the calculation in Equation 4 that shows the conductivity is inversely proportional to resistivity.

$$\sigma = \frac{1}{\rho} \qquad (4)$$

where σ is the conductivity of thin film and ρ the resistivity of thin films.

CONCLUSION

As the conclusion, the study reveals that the molar concentration of copper acetate has an influential role on the surface morphology, optical properties, thickness and electrical properties of CuO thin films. Electrical properties show current increase when the molar concentration increases. High electrical conductivity of 0.07S/m of CuO thin films were performed by sol-gel process spin-coating technique at molar concentration of 0.5M. The minimum resistivity about 12.76Ω/m has been obtained at molar concentration of 0.5M. The optical band gap of the CuO thin films were measured to be between 1.51eV and 1.9eV by using UV-vis spectrometer. For future recommendation, the molar concentration of thin film should be taken into consideration in order to get the best thin films for the devices.

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