Electrical and Optical Properties of Copper Oxide Thin Films by Sol-Gel Technique

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Abstract. Copper oxide were prepared by sol-gel technique and deposited onto quartz substrates as thin films using spin coating method. The aim of this research was to study the effects of different spin coating speeds of copper oxide thin films on the electrical and optical properties of the thin films. Five samples of copper oxide thin films with different spin coating speeds of 1000, 1500, 2000, 2500 and 3000 rpm were annealed at 600°C for 30 minutes. UV-Vis spectrophotometer and two-point probe technique were used to characterize the optical and electrical properties of the deposited films. Based on the results obtained, it revealed that the electrical conductivity of the copper oxide thin films reduce as the spin coating speeds increase. The calculated optical band gap and the resistivity of the copper oxide thin films also decrease when the spin coating speeds are increased.

1. Introduction
Copper oxide was one of the oldest and first semiconductor material that discovered and characterized, but then was overtaken by the fast development of silicon [1, 2]. Copper oxide thin films could be used for several applications in catalyst, semiconductor, solar cells [6] and electronics [7-9]. It has direct optical band gap energy in the range of 2.1 to 2.6 eV [10]. The transparent conductive copper oxide thin films had been developed by several techniques such as electrodeposition [11], thermal evaporation, sol-gel technique [12] and wet chemical method [13] which could be deposited on various substrates [14]. However, the common technique used is sol-gel method due to its simplicity, lower cost, reproducibility, ease of composition control and large area deposition [15]. In addition, sol-gel method also easily to deposit on different type of substrates that could be performed under non-vacuum environment.

Therefore in this research sol-gel method was used to form the solution of copper oxide which then deposited on quartz substrates using spin coating technique. The main goal of this paper is to study the effects of different spin coating speeds on the electrical and optical properties of the copper oxide thin films on quartz substrates. In this work, the samples were characterized using UV-Vis spectrophotometer and two-point probe method for the optical and electrical properties respectively.

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

2.1. Preparation of substrates
In this work, 2 x 2 cm$^2$ quartz substrates were used with the thickness of 0.1 cm. All substrates were cleaned using acetone, methanol and deionized water in the ultrasonic bath in order to obtain a good and clean surface contact for the next process.

2.2. Preparation of copper oxide solution using sol-gel method
In the sol-gel process, the materials used were copper acetate powder [17], diethanolamine, isopropanol and polyethylene glycol without any further purification. 0.5 molar concentration of solution was formed by dissolving 0.5 gram copper acetate powder in 9 ml isopropyl alcohol and 0.5 ml diethanolamine which act as precursor, solvent and complexing agent respectively. Then, 0.5 ml polyethylene glycol was added into the solution. Next, the copper oxide solution was stirred for 10 minutes at room temperature to achieve a transparent solution. The solution with concentration of 0.5 molar was a clear and dark blue without any suspension of particles.

2.3. Preparation of copper oxide thin films deposition by spin coating technique
Prior to the thin films deposition process, quarter area of the substrate was covered with capton tape while the other area of the substrate was left uncovered for the layer thickness measurements. After 10 minutes of stirring process, a double step spinning program was applied to obtain the homogenous precursor films. In this step, the solution was spread onto the substrates at 100 rpm for 10 seconds. The solution was spin coated with spinning speed of 1000, 1500, 2000, 2500 and 3000 rpm for 5 minutes each. Immediately after coating process, the sample was dried for 5 minutes at 250°C for each layer. Five layers of copper oxide thin films were coated one over the above. After the drying of the last layer, sample was annealed for 30 minutes at 600°C.

2.4. Samples Characterization
The absorbance and transmittance of copper oxide thin films were observed using UV-Vis spectrophotometer. I-V measurements were performed by using two-point probe technique. Prior to the I-V measurements, the thin films were coated with platinum (Pt) as the mental contacts. The sample cross section of copper oxide thin film was shown in Figure 1. The thickness of metal contacts deposited onto copper oxide thin films were 0.00006 mm while their width were 3 mm.

![Figure 1. Sample cross section of copper oxide thin film deposited by metal contacts.](image-url)
3. Results and Discussion
The results obtained from the experiment are discussed in this section.

3.1. Optical properties of copper oxide thin films
Figure 2 shows the absorbance spectra of copper oxide thin films at five different spinning rates. It could be observed that the absorbance of each film decreased with increasing of wavelength and spin coating speeds. The absorbance of the copper oxide thin film for 1000 rpm spinning rate was higher compare to the others. This due to the thin film layer thickness. The highest spin coating speed produced the thinnest film with the lowest absorbance while the lowest spinning rate produced the thickest film with the highest absorbance [20].

![Figure 2. The plot of absorbance against wavelength.](image)

The trend show here is similar with Halin et al [20]. The absorption was occurred when electron made the transition from a lower energy state in valence band to high energy state in conduction band while absorbing the excess energy as photon. It could be observed that almost absorption edge at wavelength of about 340 nm present in the spectra indicating the absorption properties of copper oxide in the UV region. The optical absorption at absorption edge related to the transition from valence band to conduction band and was closed with band gap energy [21]. Figure 3 shows the transmittances spectra of copper oxide thin films as a function of spin coating speeds.

![Figure 3. The plot of optical transmittance against wavelength.](image)
From Figure 3, it can be seen that copper oxide thin film at 3000 rpm had high transparency in the visible region (400-800nm) which was profited for transparent electronic device fabrication. While, as the spin coating speeds increased from 1000 to 3000 rpm, the transmittance was below than 70%. It can be observed that the transmittance of the light at visible region reduced when the thickness of the thin films increased [22]. Therefore, the transparency at visible region was higher in copper oxide thin films due to it had low thickness. Transmission is an inverse process of absorption where electron at conduction band moving down to a lower energy state in valence band thus annihilating the electron hole pair. The absorption coefficient, $\alpha$ was obtained using Lambert’s law as indicated by equation 1 [23, 24]:

$$
\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (1)
$$

where $t$ is the thin film thickness and $T$ is the transmittance spectrum of the thin film. Figure 4 shows all thin films exhibited a low absorption in the visible but revealed high absorption properties in the UV region (below 350 nm).

Figure 4. Relationship between absorption coefficient and wavelength.

It could be observed that copper oxide thin film at 3000 rpm had high absorption coefficient that was $6.79 \times 10^7$ m$^{-1}$ while absorption coefficient at 1000 rpm was $15.21 \times 10^6$ m$^{-1}$. It can be seen that the absorption coefficient reduced when the spin coating speeds were reduced and the thickness of the thin films were increased. Figure 5 shows the optical band gap energy that plotted using absorption coefficient, $\alpha$ data.

Figure 5. The plot of optical band gap energy versus photon energy.
The absorption coefficient, $\alpha$ of the copper oxide thin films were related to the photon energy, $h\nu$ [25], where $h\nu$ is the photon energy (eV). These optical band gap were obtained by tangent line intersection with energy axis [26] on the photon energy ($h\nu$) of the $(\alpha h\nu)^2$ versus photon energy plot. The photon energy ($h\nu$) was calculated using equation 2:

$$h\nu = \frac{hc}{\lambda}$$  \hspace{1cm} (2)

where $h$ is the Plank constant which is $6.63 \times 10^{-34}$, $c$ is the light constant that is $3 \times 10^8$ and $\lambda$ is wavelength. The optical band gap energy for these films were found to be in the range of 3.30 to 3.80 eV which were increased as the spin coating speeds increased and also were found to be affected by film thickness [20].

From the graph, the optical band gap increased when the spin coating speeds were reduced. These results somehow contradict with results reported by Halin et al [21]. Halin et al [20] explained that the decreasing in grain size of films with increasing of spinning rates will be contributed to the reduction in optical transparency trough scattering phenomenon [19, 20]. By referring the results in Table 1, it can be observed that the thickness influenced the optical band gap.

| Spin speed (rpm) | Thickness (nm) | Optical band gap (eV) |
|-----------------|----------------|-----------------------|
| 1000            | 215.43         | 3.800                 |
| 1500            | 129.92         | 3.675                 |
| 2000            | 99.65          | 3.650                 |
| 2500            | 64.53          | 3.500                 |
| 3000            | 39.97          | 3.300                 |

3.2. Electrical properties of copper oxide thin films

The I-V measurements plot for copper oxide thin films at different spin coating speeds were shown in Figure 6. In this work, Platinum (Pt) was used as the mental contacts. The I-V measurements were performed using two probe method with applied voltage -10 to 10 V. The needles of the probe must touch the surface firmly to produce reliability data.

![Figure 6. The plot of I-V curve.](image-url)
Figure 6 shows the I-V curve of copper oxide thin films at 1000, 1500, 2000, 2500 and 3000 rpm which shown that all films indicated the Ohmic behavior with linear I-V curve. It also could be observed that the current values at fixed voltage decreased due to the copper oxide thin films as spin coating speeds were increased. The increased degree of alignment of thin films after undergo the increased of spin speeds caused significant decreased in the electrical conductivity was confirmed by SEM and WAXD studies [27]. Figure 6 also shows the linear graph which obeys Ohm’s law. The current through a conductor between two points was directly proportional to the applied voltage across the two points. The current will flow and increase accordingly to the magnitude of the applied voltage as indicated by following equation 3:

\[ V = IR \]  

where \( V \) is voltage, \( I \) is current and \( R \) is resistance. From the results, it shows that all prepared samples were strongly depending on the speeds of spinning. The spectra revealed that the current at 3000 rpm was the lowest while the current at 1000 rpm was the highest among the other spectrums. As the increased of spin coating speeds, it actually helped to spread the active layer uniformly on the glass substrates [28]. As a result, the recombination process took place effectively as more holes and electrons were transported to the active area, which translated into better electrical characteristics [28].

From Figure 7, the resistivity \( \rho \), of copper oxide thin films were calculated using following equation 4;

\[ \rho = \frac{(V/I)wt}{L} \]  

where \( V \) is the supplied voltage, \( I \) is the measured current, \( w \) is the width of metal contact, \( t \) is the film’s thickness and \( L \) is the length between metal contact. The calculated resistivity obtained in this work to be 2.79, 7.54, 11.9, 43.86 and 114.57 \( \Omega \) m for thin films spin at 1000, 1500, 2000, 2500 and 3000 rpm respectively. The lowest resistivity was about 2.79 \( \Omega \) m at 1000 rpm while the highest resistivity was about 114.57 \( \Omega \) m at 3000 rpm. This was due to increase of electron and hole as carrier concentration and hence decreased the resistivity [29]. Therefore it can be seen that the lowest spin coating speeds with the thickest thin films and the increased carrier concentration produced the lowest resistivity.

![Figure 7. The plot of resistivity of copper oxide thin films versus spin coating speeds.](image-url)
The relationship between resistivity and conductivity was shown by the following equation 5;

\[
\sigma = \frac{1}{\rho}
\]

where \(\sigma\) is conductivity and \(\rho\) is resistivity values as calculated. The conductivity of the thin films in the range of 0.0087 to 0.3584 Sm\(^{-1}\). From the graph, as the spin coating speeds being increased, the conductivity of the prepared films displaying a slow down trend. This means that, the lowest spin coating speeds can improved the conductivity the thin films. Besides, the conductivity of the thin films was influenced by carrier concentration or density. It can be seen that the highest spinning rates and the highest uniformity of thin films produced the lowest conductivity of copper oxide thin films.

From the results, it can be observed that the conductivity of the thin films decreased from 1000 to 3000 rpm. The results indicated that the spin coating speed at 1000 rpm was the optimum parameter which gives the highest conductivity at 0.3584 Sm\(^{-1}\) compared to the other spin coating speeds which give lower conductivity. There were many researchers reported that the different conductivity will be affected the electron carrier mobility.

As slowest spin coating speeds were introduced, the thickest of the thin films will be generated and the carrier concentration will be higher in the thin films. This will be resulted in the increasing of the conductivity of the thin films. There were always related the conductivity, \(\sigma\) of a material to microscopic parameters that described the motion of the electrons or other charge carrying particles such as holes or ions. Besides that, the thickness of copper oxide thin films which acted as active layer were believed to be important factor to study the effect on the electrical properties [29]. The results of conductivity and resistivity with the thickness of thin films at different spin coating speeds were summarized in table 2.

| Spin speed (rpm) | Thickness (nm) | Resistivity, \(\rho\) (Ωm) | Conductivity, \(\sigma\) (Sm\(^{-1}\)) |
|-----------------|----------------|----------------------------|---------------------------------|
| 1000            | 215.43         | 2.79                       | 0.3584                          |
| 1500            | 129.92         | 7.54                       | 0.1326                          |
| 2000            | 99.65          | 11.9                       | 0.0840                          |
| 2500            | 64.53          | 43.86                      | 0.0228                          |
| 3000            | 39.97          | 114.57                     | 0.0087                          |

4. Conclusion

Copper oxide thin films were deposited on quartz substrates by spin coating technique. The thicknesses of thin films, surface topology, optical and electrical properties were investigated. In this work, the goal has been achieved to study the effects of varying the spin coating speeds of copper oxide thin films. From the results obtained, copper oxide thin film that deposited at 1000 rpm shows the highest thickness and the lowest of surface roughness. At 1000 rpm of spinning rate also shows the highest of transparency. However, at copper oxide thin film that deposited at 3000 rpm shows the lowest optical band gap. Besides, it was found that at 1000 rpm of spinning rate shows the best of electrical conductivity. Future investigation should be done on the crystallinity of the thin film by using XRD. Besides that, the investigation on the electrical and optical properties of the copper oxide thin films could be performed using doping technique.
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