Determination of the Optical Constants of CuO Using Copper (II) Sulphate Pentahydrate Complex

Daniel –Umeri Rita1*, and Ohwofosirai Adrian2**
Department of Science Laboratory Technology, Delta State Polytechnic, Ozoro, Delta State Nigeria
Department of Physics, Delta State College of Physical Education Mosogar, Delta State Nigeria.

Abstract: The transmittance of the deposited CuO thin film is very low at the UV region (200nm – 400nm) with an increasing transmittance at the visible region to a high transmittance at the near Infra red region. The optical reflectance of the film increases as wavelength increases with the highest reflectance value of about 20%. The result shows maximum refractive index of 2.5, the refractive index decreases with increasing pH values. Also seen is the increase in dielectric function with increase in photon energy is observed from the plot, further increase in the energy resulted in a decrease in the dielectric function until a constant value was obtained for all pH values. There is an increase in the optical conductivity as the pH value increases.

Keywords: Copper Oxide, pH, Optical constants, SILAR

I. Introduction

Many transition metal oxides such as copper, iron, nickel, zinc and cobalt, have several applications. One of these is cupric oxide (CuO), as an important P-type transition metal semiconductor oxide it has generated much interest due to their potential applications in optoelectronic devices. CuO a p-type semiconductor is suitable for applications in photovoltaic cells, field emission devices and batteries [1,2].

Several deposition method has being used in the preparation of CuO thin films, these include; spin coating [3], sol-gel [4], Ion beam sputtering [5], reactive evaporation [6], spray pyrolysis [7], RF sputtering, reactive magnetron sputtering [8], reactive magnetron sputtering [9], plasma evaporation [10], molecular beam epitaxy [11], and electrodeposition [12].

The successive ionic layer adsorption and reaction (SILAR) technique is a suitable method for making uniform coating for amorphous ribbons. The SILAR technique is an aqueous solution technique based on sequential reactions at the substrate–solution interface for the deposition of thin films [3]. This method is mainly based on the adsorption and reaction of the ions from the solution and rinsing between every immersion with deionised water to avoid homogeneous precipitation in the solution [4]. The method has several advantages; it does not require high quality substrates, the deposition rate and the thickness of the film can be easily controlled over a wide range with changing the deposition cycles, there are virtually no restrictions on substrate material, dimensions or its surface profile; moreover, it is convenient for large area deposition [5].

In this research work, we used the SILAR method of film deposition to report the effect of pH on the on the optical properties of the deposited film using Copper (II) sulphate pentahydrate (CuSO4.5H2O), Ammonia (NH3) and Sodium hydroxide (NaOH) as precursors.

II. Experimental Details

For the preparation of Cu4O thin film, the cationic precursor was 0.1M copper sulphate pentahydrate (CuSO4.5H2O) complex, this was obtained by dissolving 1.25g CuSO4.5H2O in 50cm3 of distilled water, while the anionic precursor was 1M sodium hydroxide (NaOH).2.0g of NaOH was dissolved in 50cm3 of distilled water to get this molarity.

Solution of copper sulphate complex was prepared by the addition of ammonia (NH3) to copper sulphate solution; this was then stirred until a deep blue solution resulted.

To deposit nanocrystalline Cu2O thin film, one SILAR cycle involves the following four steps: (i) a well-cleaned glass substrate was first immersed into cationic precursor (vessel1) (0.1M copper complex solution at pH ~8 kept at room temperature ), so the Cu2+ ions were adsorbed onto the substrate surface; (ii) then the substrate was rinsed with distilled water to remove loosely bonded Cu2+ ions from the substrate; (iii) further, the substrate was immersed into anionic precursor, so OH– ions were adsorbed and reacted with Cu2+ ions (iv) again the substrate was rinsed with distilled water to remove unadsorbed and unreacted OH– ions from the substrate. Thus, one SILAR cycle is completed. Therefore, we obtained a Cu2O film by repeating such SILAR cycles 80 times. The anionic and cationic immersion times were 20 s and the rinsing time was 10s. After deposition, the films were rinsed with copious amounts of distilled water, dried and kept in an air tight container to avoid contamination. The films were prepared for different pH values (8, 9 and 11) of the copper sulphate

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complex, both cationic and anionic precursors were kept at room temperature and 70°C respectively. The reaction occurring on the substrate surface can be represented as:

\[ \text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{CuO} + \text{H}_2\text{O} \]

III. Results and Discussion

3.1 Optical Transmittance spectra

The transmittance spectrum of samples is taken by UV-VIS Double Beam Spectrophotometer Version 6.51 in the wavelength range 200-1100 nm. Fig.1 shows the wavelength dependence transmittance of the deposited CuO thin film in the wavelength range 200nm – 1100nm.

The deposited CuO thin film is found to have very low transmittance at the UV region (200nm – 400nm) with an increasing transmittance at the visible region to a high transmittance at the near Infra red region. It is observed that the transmission spectra shift towards shorter wavelength as the particle size decreases which suggest the increase in optical energy band gap. It is supposed that the tightly adherent collides are formed with the change in micro to nano particle size [13].

![Fig. 1: Transmittance of CuO deposited at various pH](image1.png)

3.2 Reflectance of CuO thin film

The reflectance curves for the deposited CuO thin films deposited at different pH are displayed in figure 2. All the samples show low reflectance in the IR region of the electromagnetic spectrum. A careful observation of fig. 2 shows that the reflectance of the film increases as wavelength increases with the highest reflectance value of about 20%. The low reflectance exhibited by this material makes it useful for anti-reflection coating for consumer optics (spectacle lenses, camera objectives, and binoculars).

![Fig. 2: Reflectance of CuO thin film deposited at various pH.](image2.png)
3.3 Optical bandgap of the deposited CuO

The value of the optical band gap can be determined from the fundamental absorption of the material which corresponds to the excitation of electrons from the valence band to the conduction band, the absorption coefficient ($\alpha$) was directly obtained from the absorbance against photon energy (eV) values by using the relation [14].

$$\alpha = \frac{2.303 A}{t}$$

The variation of $\alpha$ as a function of $h\nu$ for CuO thin films is shown in Fig. 3a. The results indicate that $\alpha$ increases with increasing $h\nu$ for all prepared thin films. The optical bandgap energy of the products can be determined from the following equation:

$$\alpha h\nu = A \left( h\nu - E_g \right)^n$$

where $A$ is constant, $E_g$ is the optical bandgap of the material, and $n$ assumes values of $1/2$, $2$, $3/2$, and $3$ for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. For allowed direct transition, $n = 1/2$, which supports the direct bandgap nature of the semiconductor [15]. The curves of $(\alpha h\nu)^2$ versus $h\nu$ were plotted and are shown in Fig. 3b. The optical bandgap of the deposited CuO thin films are found to be 1.05eV, 1.10eV and 1.20eV for pH values of 11, 9 and 8 respectively, this indicates that the bandgap of CuO varies inversely as its pH.

![Fig. 3](image)

Fig. 3: (a) Variation of $\alpha$ as a function of $h\nu$ and (b) optical band gap of CuO thin film deposited at various pH.

3.4 The Refractive index of CuO film

The refractive index ($\eta$) is one of the fundamental properties of an optical material because of its close relationship to the electronic polarization of ions and the local field inside materials. Evaluation of the refractive indices of optical materials is considerably important for applications in integrated optic devices, such as switches, filters, and modulation, among others, in which $\eta$ is a key parameter for the device design [16]. The value of $\eta$ for thin films can be calculated from their reflectance by using simple approximations [17].

$$\eta = \frac{(1 + \sqrt{R})}{(1 - \sqrt{R})}$$

The plot for Refractive index ($\eta$) against Photon energy for CuO thin films are shown in Fig. 4. Film show maximum refractive index of 2.5, the refractive index decreases with increasing pH values.
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3.5 Dielectric Constant of the deposited CuO thin film

The dielectric function is a complex quantity and a fundamental intrinsic property of the material which consists of both the real and imaginary parts. The real part indicates how the speed of light in the material can be slowed down while imaginary part of dielectric constant is also related to conductivity so we can infer that energy lost to the metals appears as conductivity, but then it is directly proportional to conductivity otherwise conductivity plots (as function of energy again) shows structures.

Figure 5 shows the dielectric function plot against photon energy for the deposited CuO thin film with the various pH values (8, 9 and 10). A linear increase in the dielectric function with increase in photon energy is observed from the plot, further increase in the energy resulted in a decrease in the dielectric function until a constant value was obtained for all pH values.

3.6 Study of the Optical Conductance

The optical conductivity (\(\sigma\)) is obtained using the relation [13];

\[
\sigma = \frac{\alpha \eta C}{4 \pi}
\]

Where \(c\) is the velocity of light in the space; \(\eta\) is the refractive index and \(\alpha\) is the absorption coefficient.

Fig.6 shows the variation of optical conductivity with the incident photon energy. The optical conductivity increases as the pH values increase, also shown is the increase in optical conductivity with increase in photon energy. The increased optical conductivity at high photon energies is due to high absorbance of film in that region. The optical conductance and band gap indicated that the films are transmittance within the visible range [18].
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Fig. 6: optical conductivity of CuO thin film deposited at various pH.

IV. Conclusion

The deposited CuO thin film is found to have very low transmittance at the UV region (200nm – 400nm) with an increasing transmittance at the visible region to a high transmittance at the near Infra red region. The reflectance of the film increases as wavelength increases with the highest reflectance value of about 20%. The results indicate that absorption coefficient ($\alpha$) increases with increasing $h\nu$ for all prepared thin films. Film show maximum refractive index of 2.5, the refractive index decreases with increasing pH values.

The optical conductivity increases as the pH values increase, also shown is the increase in optical conductivity with increase in photon energy.

References