

Optical Analysis of Chemical bath Fabricated CuO Thin Films

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Abstract

Copper oxide CuO thin films were deposited on glass substrates using chemical bath deposition technique. The films' growth was based on the decomposition of cupric sulphate in the presence of sodium hydroxide with EDTA disodium salt ($\text{CH}_2\text{N}(\text{CH}_2\text{COOH})(\text{CH}_2\text{COONa})_2\text{H}_2\text{O}$) acting as complexing agent. Optical and morphological investigations were also performed. The films were found to have strong absorption of approximately 0.87 at wavelength range of 300-320nm. The optical absorbance generally reduced with increase in wavelength. The optical band gap of the deposited film was found to be 1.7eV.

Key words: Chemical bath Technique, Copper oxide, thin films, sodium hydroxide, Semiconductor and band gap energy.

Introduction

CuO has a relatively low bandgap (1.3-2.1 eV)¹ and is occasionally considered as an n - type semiconductor with a monoclinic structure, which is of interest on account of its potential uses in many technological fields. CuO and Cu₂O materials are known to be p-type semiconductors in general and hence potentially useful for constructing junction devices such as pn junction diodes². Apart from their semiconductor applications, these materials have been employed as heterogeneous catalysts for several environmental processes^{3,4}, solid state gas sensor heterocontacts^{5,6} and microwave dielectric materials⁷. Their use in power sources has received special attention. Thus, in addition to photovoltaic devices^{8,9}, copper oxides have been used as electrode materials for lithium batteries. The earliest studies in this area focused on their potential use as cathodes in lithium primary cells^{10,11}. CuO nanowires can also be used in p-type field effect transistors and CO gas sensors¹². A wide range of deposition techniques such as chemical vapor deposition¹³ electrodeposition¹⁴, thermal evaporation¹⁵, sol-gel techniques¹⁶, spray pyrolysis¹⁷, pulsed laser deposition¹⁸ and plasma based ion implantation and deposition¹⁹, have been used to prepare metal oxide films including copper oxide films. The present work reports the preparation and optical characterization of CuO thin films using the chemical bath deposition method. The chemical bath contains cupric sulphate and sodium hydroxide which provide Cu²⁺ and OH⁻ ions, respectively, while EDTA disodium salt acted as a complexing agent. We report the influence of complexing agent on the thickness of CuO thin films at 300K bath temperature.

Material and Methods

Experimental Details: CuO thin films were deposited on 76mm x 26mm x 1mm clean glass slide by chemical bath

deposition (CBD) technique. 10ml of 1M (CuSO₄·5H₂O) solution was measured into 5 different 50ml beaker and 10ml of NaOH solution was then added, various volumes of 1M EDTA disodium salt was then added (as indicated in table 1.1). The mixture was made up to the required volume with addition of various volumes of water. The resulting solution was stirred for a few seconds with a glass rod stirrer. A glass slide was inserted in the reaction bath and held vertically in a synthetic foam cover. The deposition process lasted 24 hours at deposition temperature of 300K. After 24 hours, the slides were taken out, rinsed with distilled water and allowed to dry in air. The slides were observed to have been coated with white deposits. The Optical absorbance spectra of the deposited films were obtained by means of UV/VIS Janway 6405 spectrophotometer. Surface morphology of the thin films deposited on glass substrate were examined by a BHZ - UMA Olumpus optical microscope. From the spectrophotometer, the absorbance in arbitrary units was measured. Parameters such as transmittance, reflectance, refractive index and extinction coefficient were then calculated using the relationship explained below:

For weakly absorbing thin film on a non absorbing substrate, the transmittance (T) can be expressed as²⁰

$$T = (1-R^2) \exp(-\alpha t), t = 1/\alpha \{ \ln(1-R^2) / T \}$$

where R is the reflectance, α is absorption coefficient, t is the thickness of the film. For semiconductors and insulators, where the extinction coefficient (k) and refractive index (n) are related as $k^2 \ll n^2$, the relationship between R and n is given by²¹ as $R = (n-1)^2 / (n+1)^2$. Also k and α are related by, $k = \alpha \lambda / 4\pi$. For weakly absorbing thin film on a non absorbing substrate, the transmittance (T) can be expressed as²⁰ $T = (1-R^2) \exp(-\alpha t)$, $t = 1/\alpha \{ \ln(1-R^2) / T \}$ where R is the reflectance, α is absorption coefficient, t is the thickness of the film. For semiconductors and insulators, where the extinction coefficient (k) and refractive index (n)

are related as $k^2 \ll n^2$, the relationship between R and n is given by²¹ as $R = (n-1)^2 / (n+1)^2$, Also k and α are related by, $k = \alpha \lambda / 4\pi$ Where λ , is the wavelength of electromagnetic radiation. In high absorption region under photon energy, the relation between absorption coefficient (α) and photon energy (hf) is given by²²: $\alpha = (hf-E_g)^n$ Where f is the frequency, h is the Planck's constant, E_g is the energy band gap and n is a number which characterizes the optical processes; $n = 1/2$ is for direct allowed transition, $n = 2$ is for indirect allowed transition and $n = 3/2$ is for forbidden direct allowed transition. When the straight portion of the plot of α^2

against hf is extrapolated to $\alpha^2 = 0$, the intercept gives the value of the transition band energy (E_g).

Table-1

Slide No.	CuSO ₄ .H ₂ O (ml)	EDTA(ml)	NaOH (ml)	Dip time(hr)
CuO(1)	10.00	0.5	10.00	24.00
CuO(2)	10.00	1.0	10.00	24.00
CuO(3)	10.00	2.0	10.00	24.00
CuO(4)	10.00	3.0	10.00	24.00
CuO(5)	10.00	4.5	10.00	24.00

Results and Discussion

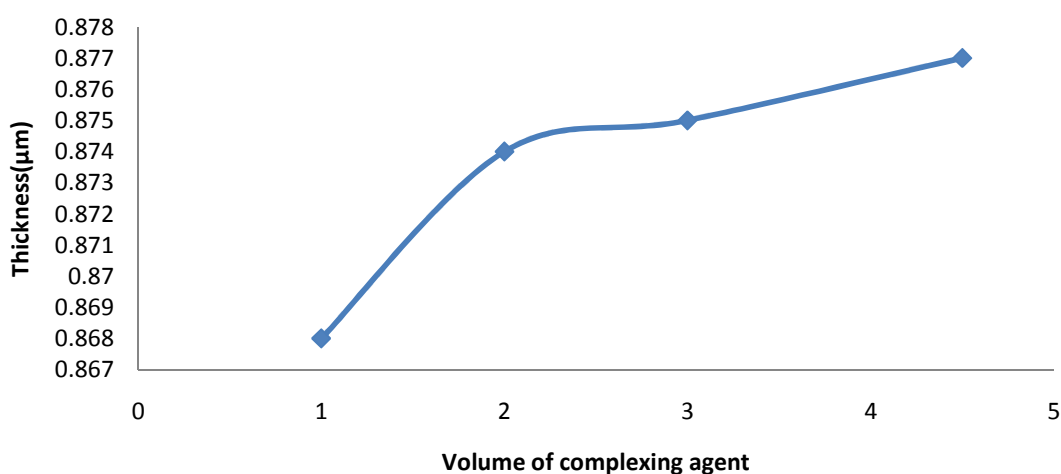


Figure - 1
Plot of thickness versus vol. of complexing agent for copper oxide thin film

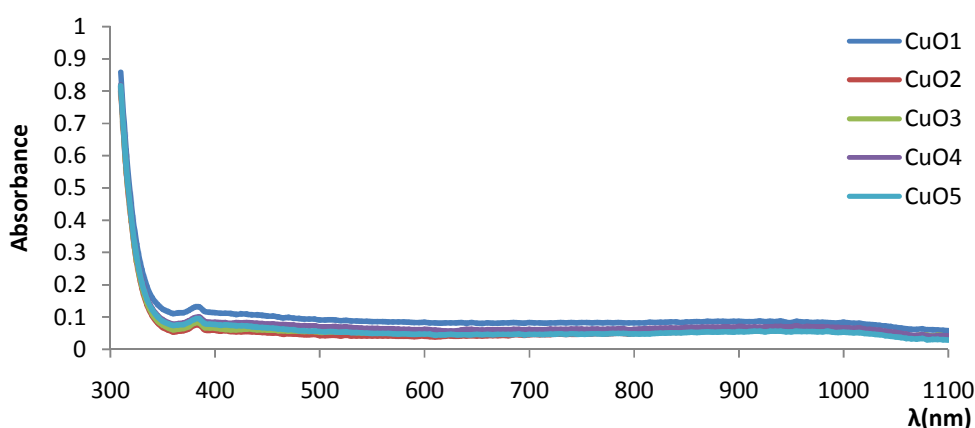


Figure - 2
Plot of absorbance versus wavelength for copper oxide thin films

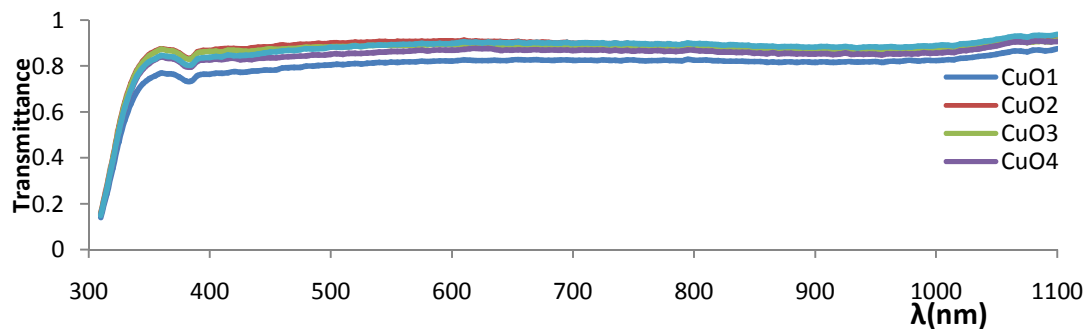


Figure – 3
Plot of transmittance versus wavelength for copper oxide thin films

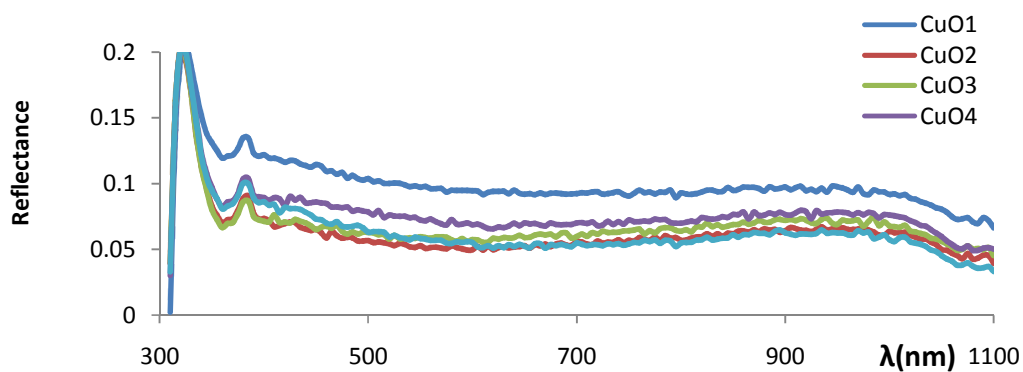


Figure – 4
Plot of reflectance versus wavelength for copper oxide thin film

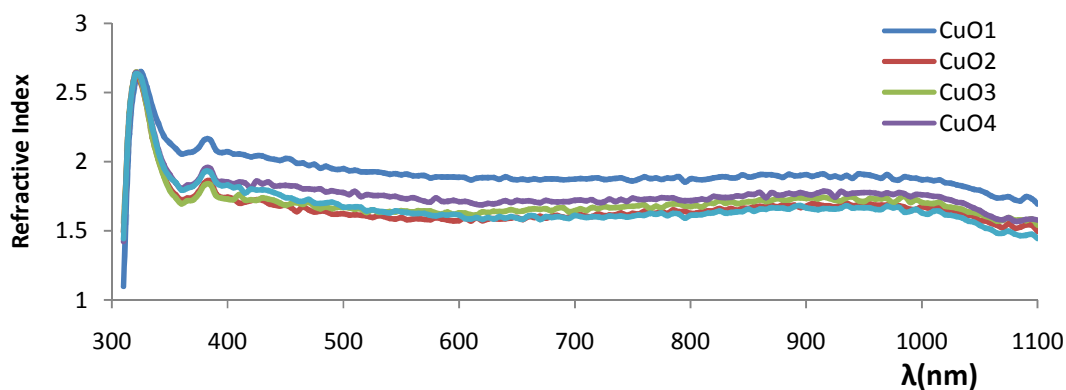


Figure – 5
Plot of refractive index versus wavelength for copper oxide thin film

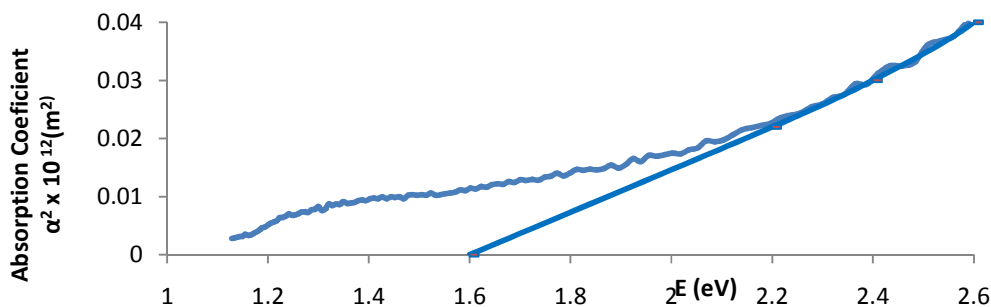


Figure – 6
Plot of absorption coefficient squared versus photon energy for copper oxide thin film

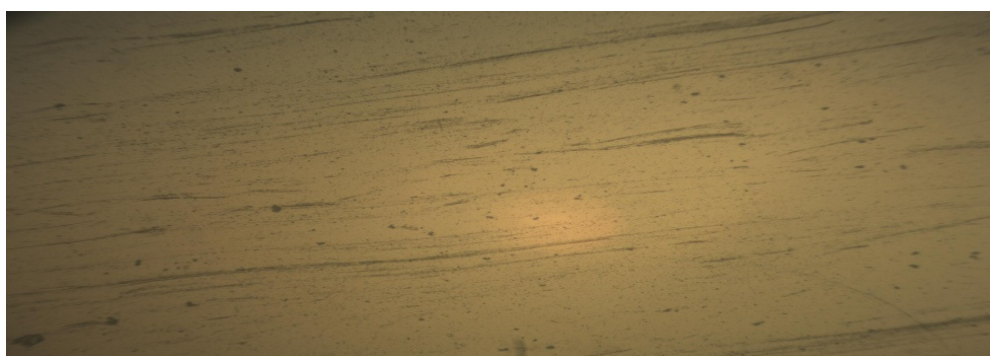


Figure – 7
Optical micrograph of copper oxide thin film

Figure 1 shows the plot of thickness versus volume of complexing agent. Figure 1 indicates that thickness increased from about 0.868 μm to about 0.877 μm with 1mls to 4.5mls volume of complexing agent. This indicates that as complexing agent has no remarkable influence on the thickness, since the thickness is approximately the same for the different volumes of complexing agent. Figure 2 and 3 show the plot of absorbance versus wavelength and transmittance versus wavelength of CuO thin films deposited in this work. The absorbance generally decreased with wavelength and has relatively low values of approximately 0.10 in the VIS/NIR region of the solar spectrum. A strong absorption of approximately 0.87 was observed at wavelength range of 300-320nm, hence the film has potential application in fabrication of solar cell. The transmittance spectrum displayed in figure 3 show increase in transmittance as the wavelength increases, all the sample have approximately 80% transmittance throughout the VIS / NIR regions. The very high transmittance in the visible region makes copper oxide films useful aesthetic window glaze materials. Also, the high transmittance of the film makes it suitable for solar energy collection because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid. Fig. 4 and 5 is a plot of reflectance and refractive index as a

function of wavelength for CuO thin films deposited in this work. Figure 4 shows an average reflectance of 0.2 (20%) in the wavelength range of 300-3200nm. This low reflectance value makes CuO thin film an important material for anti-reflection coating. Figure 5 shows the refractive index of the films. All the samples have a peak refractive index 'n' of 2.7. This result revealed that CuO thin film has high refractive index. The high refractive index possessed by CuO films make's it suitable for use as anti-reflection coatings. Fig. 6 shows a plot of α^2 versus photon energy ($h\nu$) of CuO thin films. The energy gaps for these films are obtained by extrapolating the linear part of the curve to the energy axis. It is observed from the figure that CuO thin film exhibits direct band transition and the band gap of 1.6 eV. This is in close agreement with the finding of²³, who reported a band gap of 1.3eV,²⁴, who reported a band gap range of 1.0eV–1.4 eV and²⁵,who reported a band gap range of 1.21–1.51 eV, The surface microstructure of CuO film (shown in fig.7) were viewed using a BHZ - UMA Olympus optical microscope at a magnification of x100. The optical micrographs of the CuO show high density of grains. The high density of these grains implies that the nucleation has occurred on all sites. It shows uniformity in the distribution of the grains, the grains are small and regular.

Conclusion

The fabrications of CuO thin film with band gap of 1.7 have been successfully carried out using chemical bath deposition technique at 300K. The films were found to have strong absorption of approximately 0.87 at wavelength range of 300-320nm and depreciates as the wavelength increased. Generally all the samples have approximately 80% transmittance throughout the VIS/NIR regions and an average reflectance of 20% in the range of 300-320nm. The optical micrographs of the CuO show high density of grains and uniformity in the distribution of the grains, the grains are small and regular.

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