Optical Properties of Cuprous Oxide Thin Film Prepared by Chemical Bath Deposition Technique

D.D.O. Eya[1], Ph.D., A.J. Ekpunobi[2], Ph.D., and C.E. Okeke[3], Ph.D., FAS

[1] Department of Physics, Federal University of Techology, Owerri, Nigeria
E-mail: eyadom2003@yahoo.com
[2] Department of Industrial Physics, Nnamdi Azikiwe University, Awka, Nigeria
[3] Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria.

ABSTRACT

Cuprous oxide (Cu_2O) thin films have been prepared by a simple and highly reproducible chemical bath deposition technique and were thermally treated under various annealing temperatures up to 523K. The films show very high transmittance (80 –95%) in the visible/near infra-red regions of the electromagnetic spectrum, thereby making the oxide film a very good material for warming applications especially in temperate regions. The absorbance and reflectance are generally low (<10%), dwindling with longer wavelengths. The band gap of the oxide films is in the range of 2.65 – 2.70eV; the value showing limited variation with annealing temperatures and bath concentration. The maximum value of the refractive index within the temperature range is 2.63.

(Key words: cuprous oxide, Cu_2O, optical properties, thin film, chemical bath deposition, annealing temperature, band gap, PACS Nos: 81.10.Dn, 82.30.Fi, 78.66.-w, 78.20.Ci)

INTRODUCTION

Cuprous oxide (Cu_2O) thin film is a colored film ranging from yellow to red-brown [1-2]. Although there is limited literature available on these films, one report shows a direct band gap of 1.95eV for Cu_2O, which does not ideally match the solar spectrum. However, interest in this material stems from the possibility of extremely low production costs, albeit at low conversion efficiency [3].

In recent times, there have been several techniques adopted for thin film deposition such as atmospheric chemical vapor deposition [4], ionized cluster beam deposition [5], DC reactive magnetron sputtering [6], pulsed laser deposition [7], chemical bath deposition [8-12], and others. Many of these methods are expensive and require a high vacuum environment [14]. The chemical bath technique has frequently been used for the deposition of metal oxide thin films [3,8,13]. The technique has also been used widely to deposit other materials [9,11].

The choice of this technique centers largely on the fact that it possesses a number of advantages over conventional thin film deposition methods, such as low cost, low temperature, and easy coating of large surfaces. This technology is based on the controlled release of the metal ions. In the case of oxide films, the deposition follows a two-step process: deposition of the hydrous film and its pyrolytic decomposition into the anhydrous film [10].

In this paper, we report on the preparation and optical properties of cuprous oxide thin film, on a microscope glass slide substrate, using a chemical bath deposition technique.

EXPERIMENTAL DETAILS

In this study, the Cu_2O thin films were prepared using the chemical bath deposition technique. The following constitutes the chemical bath system for optimum deposition: 20ml of 0.1M copper nitrate [$Cu(NO_3)_2$], 20ml of 0.1M Hydrazine (NH_2NH_2), and 5.5ml of 1M triethanolamine (TEA) which is the complexing agent.

To obtain these solutions, 9.664g of $Cu(NO_3)_2.3H_2O$ was dissolved in 400ml of distilled water, 1.23ml of NH_2NH_2 was mixed with 400ml of distilled water, and 27.3ml of TEA with 200ml of distilled water each time. Several bath compositions were employed but the optimum result was achieved with the specifications noted above. Equally good uniform depositions were obtained using 0.2M, 0.05M and 1M solutions, respectively.

Solutions for the deposition bath were made in 50ml beakers and 76mm x 26mm x 1mm commercial–quality glass microscope slides were used as the substrate. Before use, these glass slides were soaked in a solution of nitric acid and hydrochloric acid and then washed thoroughly with detergent and rinsed in distilled water.

After transferring the solution to a beaker, the substrate was suspended vertically in the solution with the aid of a beaker cover. The addition of the 1M TEA to $CU(NO_3)_2$ solution resulted in a deep blue solution. The further addition of NH_2NH_2 to the solution resulted in a hissing sound which signaled the release of nitrogen gas and a rapid change in color, first to light blue and then to light yellow, reddish brown, and, finally, blue.

The optimum growth period is in the range of 4-5 hours. The film deposited is either pure yellow or reddish brown but gradually turns yellow with time.

$$Cu(NO_3)_2 + TEA \longleftrightarrow [Cu\ (TEA)]^{2+} + 2NO^-_3$$

$$[Cu\ (TEA)]^{2+} \longleftrightarrow Cu^{2+} + TEA$$

$$NH_2NH_2 + 2NO^-_3 + 6e^- \longleftrightarrow 2H_2O + 2N_2 + 4O^{2-}$$

$$8Cu^{2+} + 4O^{2-} + 8e^- \longleftrightarrow 4Cu_2O\downarrow$$

Some of the resulting thin films were annealed at temperatures 453 and 523K.

The composition of the thin Cu_2O films was analyzed by undertaking an energy dispersive X-ray fluorescence (EDXRF) study of the samples in which a $25mCi\,^{109}Cd$ excitation source that emits Ag –k X –rays (22.1KeV) was used. The optical absorbance/transmittance of the films were studied in the spectral range of 340 –1000nm using a Unicam Helios Gamma UV-Visible Spectrophotometer.

RESULTS AND DISCUSSION

It was observed that most of the films removed from the reaction bath earlier than the optimum period of deposition (4-5 hours) were not uniform. If the films are left in the solution much longer than the optimum period, certain bluish deposition interferes with the desired deposit.

In the beginning of the deposition process, the ionic product of the solution (IP) is greater than the solubility product of the solution (SP), which leads to film deposition. As the ions (cations and anions) react, the IP decreases with time up to the moment when it becomes equal to the SP [9]. This is the point at which the yellow/red – brown component of the solution has either been deposited on the substrate or the side of the beaker or has formed sediment leaving a light blue solution.

The EDXRF of the deposited films showed energy of 8.041KeV corresponding to peak intensity of 1.216c/s for copper (Table 2). Table 2 shows the details of the EDXRF analysis for sample $k_{21.}$ Other samples, on the average, show the same details. The presence of oxygen could not be detected by the X-ray source. The results of the analysis are shown in the tables below.

Figure 1 shows the spectral dependence of the transmittance/reflectance of the Cu_2O thin films under annealing temperatures of 453 and 523K. In the UV region (<400nm), most of the light is either reflected or absorbed. Transmittance is negligible in the region.

Near the UV-VIS boundary of the visible region, the transmittance rises sharply over a short range of wavelengths and then increases slowly over the rest of the wavelengths. The maximum and minimum values of transmittance recorded are 39.4 and 88.1% respectively.

On the other hand, the reflectance decays exponentially with increasing wavelength between 6.4% and 20.1%. The high transmittance of the Cu_2O thin film in the visible/infra-red regions makes the film a very good material for warming applications in homes in temperate regions of the globe and in agricultural applications especially in poultry farms.

Table 1: Energy dispersive X-ray fluorescence of blank glass substrate (as reference).

ELEMENT	ENERGY [KEV]	INTENSITY [c/s]	SENSITIVITY	GEOMETRY	CONC. [FRAC]	ERROR
Cd	3.130	0.065	2.25E+02	0.0022	1.30E-01	-LOD-
K	3.312	0.052	1.26E+03	0.0025	1.57E-02	-LOD-
Sn	3.440	0.001	3.07E+02	0.0028	9.02E-04	-LOD-
Ca	3.690	0.362	1.50E+03	0.0023	1.03E-01	4.49E-03
I	3.930	0.040	1.04E+03	0.0024	1.58E-02	-LOD-
Ti	4.508	0.031	3.44E+03	0.0026	3.39E-03	-LOD-
V	4.949	0.032	5.16E+03	0.0032	1.86E-03	-LOD-
Cr	5.411	0.040	6.70E+03	0.0040	1.44E-03	-LOD-
Fe	6.400	0.085	1.05E+04	0.0062	1.27E-03	1.82E-04
Co	6.925	0.045	1.31E+04	0.0076	4.36E-04	-LOD-
Ni	7.472	0.035	1.63E+04	0.0093	2.26E-04	-LOD-
Cu	8.041	0.035	1.92E+04	0.0112	1.61E-04	1.09E-04
Zn	8.631	0.043	2.30E+04	0.0133	1.38E-04	4.34E-05
Ga	9.243	0.039	2.53E+04	0.0158	9.59E-05	3.34E-05
As	10.532	0.060	3.26E+04	0.0216	8.27E-05	3.12E-05
Se	11.210	0.047	3.67E+04	0.0250	4.97E-05	-LOD-
Pb	10.540	0.051	1.91E+04	0.0217	1.21E-04	-LOD-
Br	11.907	0.042	4.54E+04	0.0287	3.15E-05	-LOD-
Rb	13.375	0.045	4.94E+04	0.0369	2.40E-05	-LOD-
Sr	14.142	1.037	5.37E+04	0.0414	4.55E-04	-LOD-
Y	14.933	0.198	5.81E+04	0.0461	7.24E-05	-LOD-
Zr	15.746	0.745	7.47E+04	0.0509	1.91E-04	1.10E-05
Nb	16.584	0.073	8.11E+04	0.0558	1.58E-05	4.42E-06
Mo	17.443	0.111	8.76E+04	0.0608	2.03E-05	4.16E-06

SAMPLE: IS6594, MATRIX: [AO(RES) = 11000], WEIGHT [g/cm^2]: 1.048; Blank

Table 2: Analysis results for energy dispersive X-ray fluorescence of substrate with Cu_2O film.

	ENERGY [KEV]	INTENSITY [c/s]	SENSITIVITY	GEOMETRY	CONC. [FRAC]	ERROR
Cd	3.130	0.044	2.25E+02	0.0021	8.90E-02	-LOD-
K	3.312	0.033	1.26E+03	0.0025	1.03E-02	-LOD-
Sn	3.440	0.001	3.07E+02	0.0027	9.13E-04	-LOD-
Ca	3.690	0.248	1.50E+03	0.0025	6.38E-02	4.49E-03
I	3.930	0.036	1.04E+03	0.0027	1.25E-02	-LOD-
Ti	4.508	0.032	3.44E+03	0.0032	2.83E-03	-LOD-
V	4.949	0.030	5.16E+03	0.0039	1.46E-03	-LOD-
Cr	5.411	0.032	6.70E+03	0.0049	9.49E-04	-LOD-
Fe	6.400	0.042	1.05E+04	0.0076	5.15E-04	1.82E-04
Co	6.925	0.037	1.31E+04	0.0093	2.97E-04	-LOD-
Ni	7.472	0.036	1.63E+04	0.0114	1.89E-04	-LOD-
Cu	8.041	1.216	1.92E+04	0.0137	4.53E-03	1.09E-04
Zn	8.631	0.088	2.30E+04	0.0164	2.28E-04	4.34E-05
Ga	9.243	0.048	2.53E+04	0.0190	9.73E-05	3.34E-05
As	10.532	0.115	3.26E+04	0.0260	1.33E-04	3.12E-05
Se	11.210	0.043	3.67E+04	0.0301	3.83E-05	-LOD-
Pb	10.540	0.056	1.91E+04	0.0260	1.10E-04	-LOD-
Br	11.907	0.045	4.54E+04	0.0345	2.82E-05	-LOD-
Rb	13.375	0.047	4.94E+04	0.0444	2.08E-05	-LOD-
Sr	14.142	0.061	5.37E+04	0.0498	2.25E-05	-LOD-
Y	14.933	0.223	5.81E+04	0.0554	6.77E-05	-LOD-
Zr	15.746	0.747	7.47E+04	0.0613	1.60E-04	1.10E-05
Nb	16.584	0.074	8.11E+04	0.0673	1.33E-05	4.42E-06
Mo	17.443	0.122	8.76E+04	0.0734	1.86E-05	4.16E-06

SAMPLE: IS6592; MATRIX: [AO(RES) = 11000]; WEIGHT [g/cm^2]: 1.048; K21

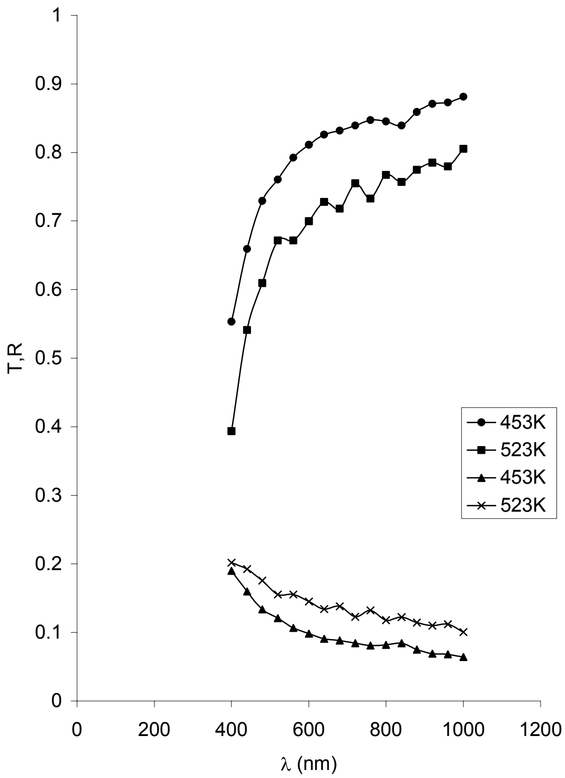

Figure 1: Transmittance (T) and Reflectance (R) as functions of wavelength (λ) under various thermal treatments.

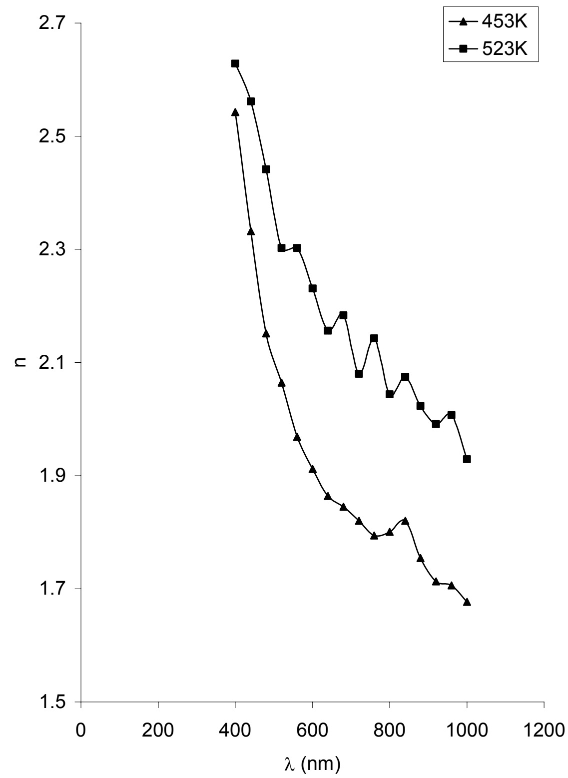

Figure 2: Refractive index (n) as a function of wavelength (λ) under various thermal treatments.

The reflectance at normal incidence can be expressed in terms of the optical constants, (n) and (k) as [16]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad \text{..............................} \ (1)$$

Where (n) is the refractive index and (k) is the extinction coefficient. In the range of frequencies in which the films are weakly absorbing, $k^2 << (n-1)^2$ so that:

$$R = \frac{(n-1)^2}{(n+1)^2} \ \text{, or}$$

$$n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \quad \text{................................} \ (2)$$

Values of the refractive index were calculated using equation (2). Figure 2 shows the variation of refractive index, (n) of the films within a given wavelength. The values decay exponentially with increasing wavelength. This indicates that the electromagnetic radiation passing through the material is slower in the UV and VIS regions near the UV-VIS boundary. However, the speed is higher in the VIS and near infra-red (NIR) regions. The maximum value of n recorded is 2.63 and the minimum value is 1.68 as shown in the figure.

For non-magnetic materials, the square of refractive index is the dielectric constant. The complex dielectric constant is given by the following equation:

$$\varepsilon = \varepsilon_r + \varepsilon_i = (n + ik)^2 \ \text{..........................} \ (3)$$

Where ε_r and ε_i are the real and the imaginary parts of ε and $(n + ik)^2$ is the complex refractive index. From equation (1), we obtain:

$$\varepsilon_r = n^2 - k^2 \quad \text{and} \quad \varepsilon_i = 2nk \ \text{..................} \ (4)$$

Equation (4) was used in calculating the real and imaginary dielectric constants. The real and imaginary dielectric constants as function of the wavelength are shown in Figures 3 and 4 respectively. Both show exponential decay with

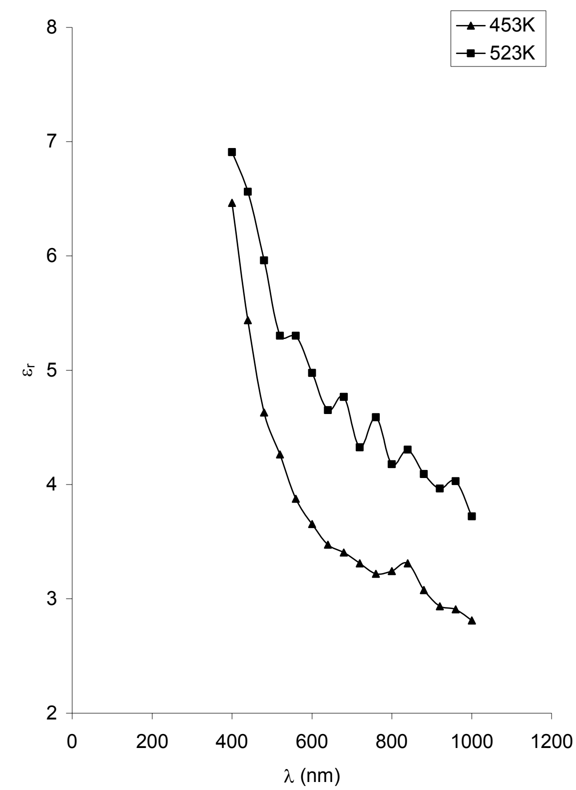

Figure 3: Variation of real dielectric constant with wavelength under various thermal treatments.

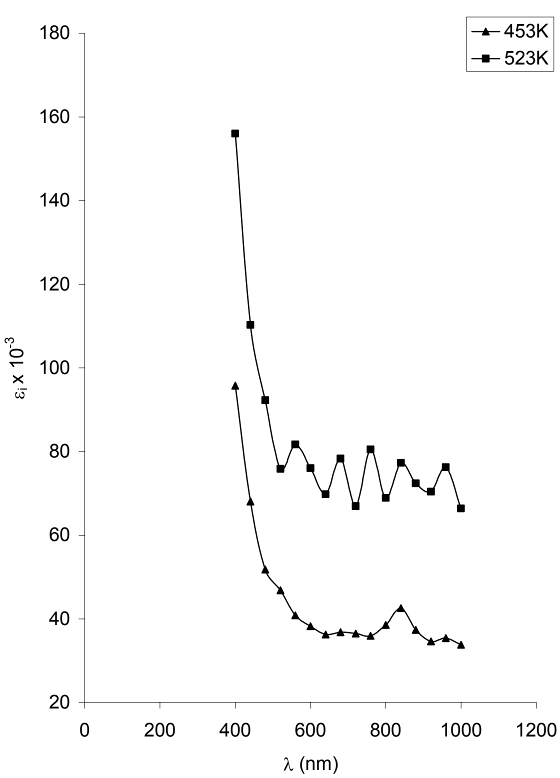

Figure 4: Variation of imaginary dielectric constant with wavelength under various thermal treatments.

increasing wavelength from very high values in the UV region. The maximum value obtained for them are 6.95 and 15.6 x 10^{-3} and minimum values 2.45 and 2.1 x 10^{-3} respectively.

Figure 5 shows the spectral dependence of the absorbance of the films annealed at various temperatures. The figure shows that absorbance also decays exponentially with an increase in wavelength. The absorbance is very large in the UV regions but decays very sharply within the UV-VIS boundary extending into the VIS region. The decay becomes relatively slower in the VIS and NIR regions.

The absorption coefficient α of the oxide film is related to the photon energy $h\nu$ by the following:

$$(\alpha h\nu) = (h\nu - E_g)^{1/2}$$

$$(\alpha h\nu)^2 = (h\nu - E_g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where (h) is Plank's constant and (ν) is the photon frequency.

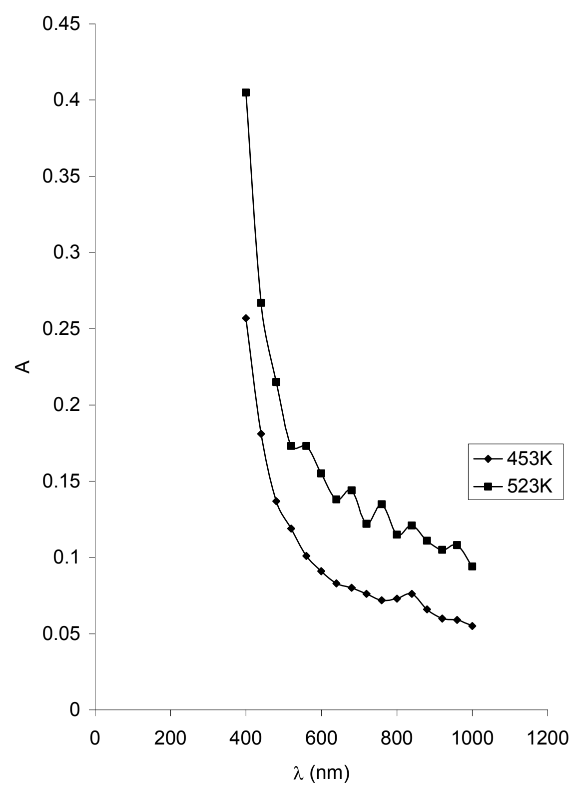

Figure 5: Absorbance (A) as a function of wavelength (λ) under various thermal treatments.

The band gap (E_g) of the film was obtained when the straight portion of the $(\alpha h\nu)^2$ versus $h\nu$ plot is extrapolated to $(\alpha h\nu)^2 = 0$ (12,15) as shown in Figure 6.

A band gap range of 2.65 –2.70eV was obtained for the annealed samples of Cu_2O thin film as shown in Figure 6. The range corresponds to a wavelength range of 4.69 x 10^{-7} – 4.21x10^{-7}. The observed variation in the value of the band gap of the oxide films is an indication of the effect of annealing and difference in molar concentration on the properties of the semiconductor. Table 3 shows the band gaps of the oxide films as a function of annealing temperature. The table shows a decrease in band gap with increasing annealing temperature.

The only report on Cu_2O in the literature reported a band gap for the film as 1.95eV [3]. Though the values of the band gap do not match the solar spectrum, Cu_2O has been found to be a useful material to provide Shottky barriers in conjunction with copper layers in solar cells. In view of the brilliant color of the film, it could also be used for aesthetic glaze coatings.

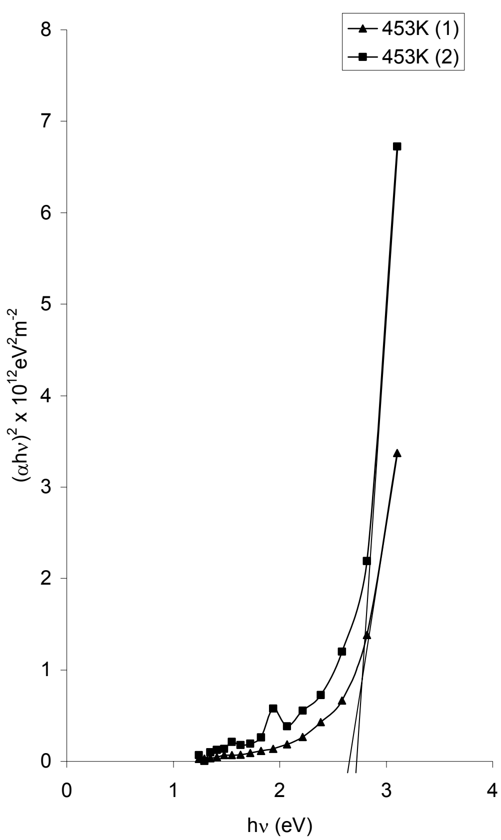

Figure 6: A plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for Cu_2O

Table 3: Band Gap as a Function of Annealing Temperature.

Sample	Annealing Temperature (K)	Band gap(eV)
K_7	300	2.95
K_{21}	300	2.95
K_3	423	2.95
K_9	453	2.65
K_{10}	453	2.70
K_{14}	523	2.70

CONCLUSION

Cuprous oxide thin films have successfully been grown by the chemical bath deposition technique using copper nitrate [$Cu(NO_3)_2$] and Hydrazine (NH_2NH_2) with TEA as the complexing agent.

The band gap of the film is 2.70eV. Annealing is necessary to remove any water molecules that may interfere with the properties of the film. The oxide films were annealed at various temperatures up to 523K. Cu_2O films show high transmittance in the visible/infra-red regions of the electromagnetic spectrum but either reflect or absorb most of the electromagnetic radiation in the UV region.

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ABOUT THE AUTHORS

D.D.O. Eya, Ph.D. is an academic staff member in the Department of Physics at the Federal University of Technology in Owerri, Nigeria. His research interests are in the areas of photovoltaics, thin film deposition, and characterization.

A.J. Ekpunobi, Ph.D. serves as the Head of the Department of Industrial Physics at Nnamdi Azikiwe University in Awka, Nigeria. His research interests include photovoltaics, thin film deposition and characterization, and optical technology.

C.E. Okeke, Ph.D., FAS is a professor of Solid State Physics and a member of the academic staff of the Department of Physics and Astronomy at the University of Nigeria, Nsukka. His research interests include photovoltaics, thin film deposition and characterization, and biomass energy conversion.

SUGGESTED CITATION

Eya, D.D.O., A.J. Ekpunobi, and C.E. Okeke. 2005. “Optical Properties of Cuprous Oxide Thin Film Prepared by Chemical Bath Deposition Technique”. *Pacific Journal of Science and Technology*. 6(2):98-104.

Pacific Journal of Science and Technology