Optical Properties in CuCl Binary Thin Films Deposited by Solution Growth Method

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ABSTRACT

Cuprous Chloride (CuCl) binary thin films were grown on glass substrates at 300 K by electroless (solution-growth) method. The as-grown films were characterized for elemental composition using the energy dispersive X-ray fluorescence (EDXRF) and colorimetric methods The optical constants (i.e. the index of refraction n, the extinction coefficient k, the and absorption coefficient a) were determined using the absorption A, the transmission T, and the reflection R, at normal incident of light in the wavelength range of 200-850 nm The film has fairly high absorption in the UV region but very high absorption in the VIS region of about 400 – 700 nm. The high absorbance of the film made it a good material for large area selective coatings for photothermal conversion of solar energy. The average index of refraction is 2.07 and the average extinction coefficient is 7.81 x 10^{-2}. The index of refraction of n > 2.0 makes the material a good candidate for protective coatings. The plot of $(\alpha h\nu)^2 = f(h\nu)$ showed that the material is a direct band gap material, with a band gap of about 2.20 eV. This material could also be used in selective coatings for the photothermal conversion of solar energy due to their high absorbance and for protective coatings.

(Key words: film, electroless, optical constants, optical band gap, coatings)

INTRODUCTION

Cuprous Chloride (CuCl) is a white cubic crystal with density (specific gravity) of 4.14, melting point of 43 C, and boiling point of 149 C. It becomes greenish on exposure to light. It is slightly soluble in water, soluble in acids, ammonia, ether, and insoluble in alcohol and acetone. It is used as catalyst, preservative and fungicide, de-sulfurizing and de-colorizing agent in the petroleum industry, and as an absorbent for carbon monoxide (Lewis, 1993). This material in thin film form, as revealed by our studies, could be used in electronic industry for the manufacture of capacitors due to their high dielectric constant. High dielectric constant materials are widely used in the manufacture of multi-layer capacitors (MLCs) (Appiagyei, 1998). In thin film form, the material will increase miniaturization and the volumetric efficiency. The cost effectiveness in producing the material is also enhanced by the use of electroless (solution-growth) method.

THEORY AND CALCULATIONS

A beam of photons incident on a material of thickness x and density r undergoes absorption A, transmission T, and scattering S, or reflection R. The mass attenuation for compounds, mixtures, alloys of elements A, B, C, … in concentrations C_A, C_B, C_C, … is expressed by

$$(\mu/\rho)x,\lambda = \sum_{i=1} Ci(\mu/\rho)i,\lambda$$

$$= C_A\,(\mu/\rho)_{A,\lambda} + C_B\,(\mu/\rho)_{B,\lambda} + \ldots$$

where (m/p)μ,λ is the mass absorption coefficient of compound A at wavelength λ.

Alternatively, the attenuation inside the material is expressed by the Lambert-Beer-Bouguer law (Ballard, et al, 1972; Ezekoye, 2001):

$$I = Io\exp(-\alpha x)$$

where I is the intensity of the photons at a distance x inside the material, Io is the intensity just inside the front surface and, α is absorption coefficient.

The absorbance (A) of the material is obtained directly by measurement and is given by Ezekoye, 2001 and Ajayi, et al, 2002. The absorption coefficient, α, is the fractional decrease in intensity per unit increase in distance. The absorption coefficient is related to other optical as follows (Pankove, 1971; Hass, 1972; Wooten, 1972; Animalu, 1977; Sze, 1981 and Soliman, 1998):

$$\alpha = 2\omega k / c = 4\pi k / \lambda ,$$

and,

$$k = \alpha\lambda / 4\pi ,$$

where λ is the wavelength of the photons, ω is the angular frequency and k is the extinction coefficient.

The absorption coefficient α is computed at any given wavelength using the above equation (Soliman, 1998).

The optical conductivity σ is related absorption coefficient α by (Pankove, 1971 and Ezekoye, 2001):

$$\alpha = 4\pi\sigma / nc$$

The complex dielectric constant εc is related complex index of refraction nc and thus extinction coefficient by (Pankove, 1971 and Ezekoye, 2001):

$$\varepsilon_c = (\varepsilon_1 - i\varepsilon_2) = n_c^2 = (n + ik)^2$$

By the plot of $(n^2-1)^{-1}$ verses λ^{-2}, one can also obtain the complex dielectric constant from the point of intersection of the linear parts with ordinate (Soliman, 1998).

Close to the absorption edge the absorption coefficient α is given by (Pankove, 1971; Sze, S.M.1981; Chopra and Das, 1983):

$$\alpha = (h\upsilon - Eg)^{\gamma},$$

where $h\nu$ is the energy of the photon, Eg is the band gap, γ is a constant. The constant γ =1/2 for all allowed direct photon transitions and 3/2 for forbidden direct transitions. It is γ = 2 for indirect optical transitions and ½ for all allowed indirect transitions to excitation states.

The plot of α^2 against $h\upsilon$ was used to obtain the band gap of the material (Figure.3.). The linear portion was extrapolated to the point where α = 0, giving, $h\upsilon$ = Eg. One can also plot a graphical representation of $(\alpha h\nu) = A(h\nu - E_g)^{\gamma}$, were A is a constant (Soliman, 1998).

EXPERIMENTAL METHODS

The starting materials for the preparation of the good quality binary thin films of CuCl on glass substrate at 300 K include copper sulphate ($CuSO_4.5H_2O$), potassium chloride (KCl), Ammonia (NH_3), MERK and highly purified distilled water. Ammonia (NH_3) was used as complexing agent to slow down the reaction to avoid instantaneous precipitation.

The optically flat glass substrates were thoroughly washed by degreasing in aqua-regia (a mixture of HCl and HNO_3 in 3:1 ratio) for about twenty-four hours (24h), washed with detergent, rinsed in distilled water and dried in air. The substrates were inserted vertically and allowed to stand for various times. The various growth parameters such as molar and volume concentrations, pH and time were altered accordingly in order to stabilize and optimize the growth. The substrates were removed from the bath after some predetermined time, rinsed with distilled, well-labeled and dried in air. The reaction is follows:

$CuSO_4.5H_2O \leftrightarrow Cu(NH_3)_4)]^{2+} + SO_4^{2-}$

$[Cu(NH_3)_4)]^{2+} \leftrightarrow Cu^{2+} + NH_3$

$KCl \leftrightarrow K^+ + Cl^-$

$Cu^+ + Cl^- \leftrightarrow CuCl$

Details of the variations of the bath parameters are shown in Table 1.

Table 1: Preparation of Copper Chloride (CuCl) at 300 K.

CC	Dep. Time (Hr.)	$CuSO_4.5H_2O$ (M)	Vol (ml)	KCl Mol (M)	Vol (ml)	NH_3 Mol (M)	(ml)	H_2O (ml)	pH
1.11	60	0.5	5	0.4	10	10	2	15	10
1.21	62	0.5	5	0.4	10	10	2	15	10
1.31	76	0.5	5	0.4	10	10	2	15	10
1.41	84	0.5	5	0.4	10	10	2	15	10

The as-grown films were characterized for optical properties using a double beam spectrophotometer machine (PYE UNIC AM 8 – 100, $\Delta\lambda \pm 0.1$nm).

RESULTS AND DISCUSSION

The as-grown films have good mechanical and chemical adhesion to the glass substrate. Elemental composition studies using the energy dispersive X-ray fluorescence (EDXRF) and colorimetric method show the as-grown film is non-stoichiometric and is rich in copper.

The thickness of the material ranged from 0.70-0.93 microns. The film has fairly high absorption in the UV region but very high absorption in the VIS region of about 400 – 700 nm. The high absorbance of the film makes it a good material for large area selective coatings for photothermal conversion of solar energy. The material has mean absorption coefficient of 2.13×10^6 m^{-1}.

The transmittance-reflectance spectra are shown in Figure 1. The transmittance spectrum showed peak of about 28% of photon energy at about 250 nm and a minimum of about 4%. The material has a relatively low transmittance in the wavelength range of 200-650 nm.

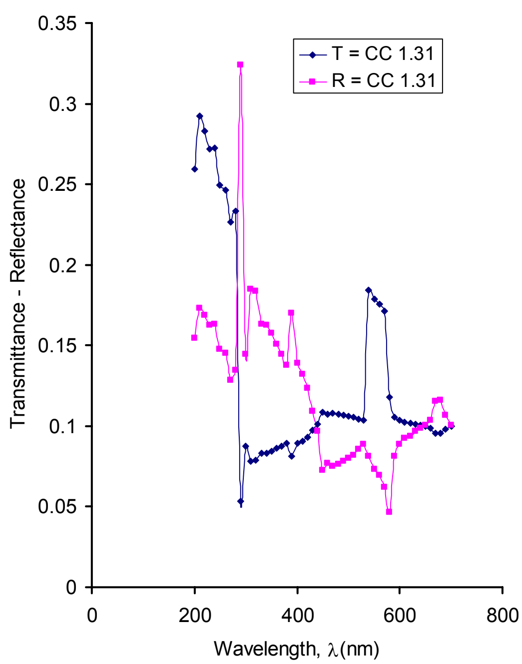

Fig. 1: Transmittance - Reflectance Spectra of CuCl Film prepared at 300K.

The reflectance ranged from a maximum of about 35% to a minimum of about 4%. The reflectance is relatively low. These observations are confirmed since the material has high absorbance throughout UV/VIS/NIR.

The plot of index of refraction n and extinction coefficient k against the photon energy is shown in Figure 2.

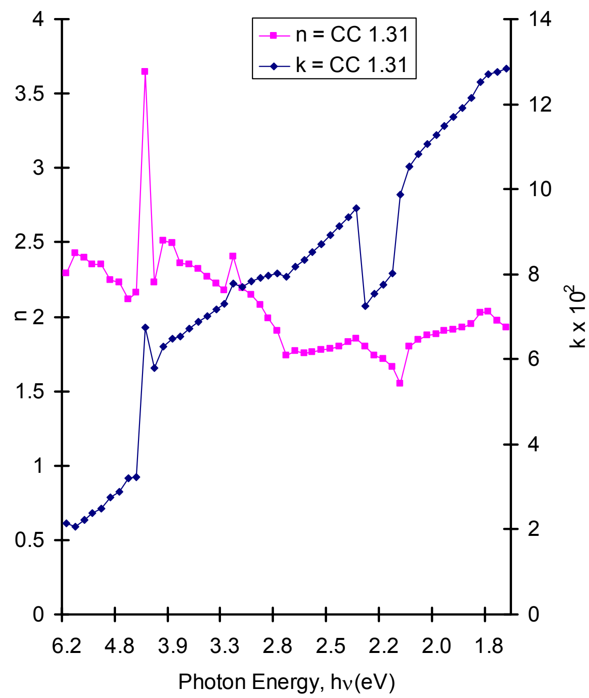

Fig.2: Plots of Refractive Index n and Extinction Coefficient k against Photon Energy for CuCl Film prepared at 300K.

The average index of refraction is 2.07 while the optimum value is about 3.70. The sharp peak occurred at photon energy of about 3.80 eV. The extinction coefficient k varied continuously from a minimum of about 2.20×10^2 to a maximum of about 13.0×10^2. The average extinction coefficient is about 7.81×10^{-2}. The index of refraction of n > 2.0 makes the material a good candidate for protective coatings for anti-dazzling, poultry protection, coatings of eyeglasses, computer and TV screens.

Figure 3 shows the plot of real dielectric constant and imaginary dielectric constant versus the photon energy. The average real dielectric constant is 4.38 and average imaginary dielectric constant is 0.31. The peak of real dielectric constant occurred at the photon energy level of about 4.00 eV with the value of 13.0. This value of dielectric constant is quite high. The peak value of imaginary dielectric constant occurred at the same photon energy with a value of about 0.52 (Figure 3).

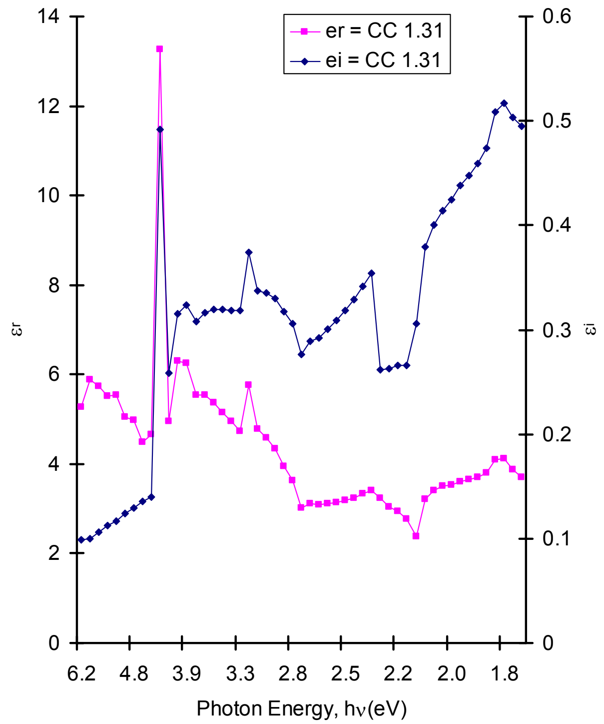

Fig.3: Plots of Real Dielectric Constant ε_r and Imaginary Dielectric Constant ε_i against Photon Energy for CuCl Film Prepared at 300K.

Normal dispersion is associated with an increase in ε_r with hν. Anomalous dispersion is associated with decrease in ε_r with hν (Figure 3). Normal dispersion is seen to occur everywhere except in the neighborhood of resonant frequency and only where there is anomalous dispersion is the imaginary part of ε appreciable (Jackson, 1975; Jenkins and White, 1976). Since a positive imaginary part to ε represents dissipation of energy from the electromagnetic wave into the medium, the regions where ε_i is large is called the region of resonant absorption. The high values of the dielectric constant make this material good for the manufacture of capacitors in electronic industry. In the thin film form such materials could be used for multi-layer capacitors (MLCs) which will enhance further miniaturization

The plot of $(\alpha h\nu)^2 = f(h\nu)$ shows that the as-grown film has a direct band gap with a band gap Eg of about 2.20 eV (Figure 4.). The band gap is within the range of 1-5 eV which falls in the range of semiconductors. The material in thin film form could serve in photocell and also in solid-state detector applications, which works on the same principle (Young and Freeman, 1996).

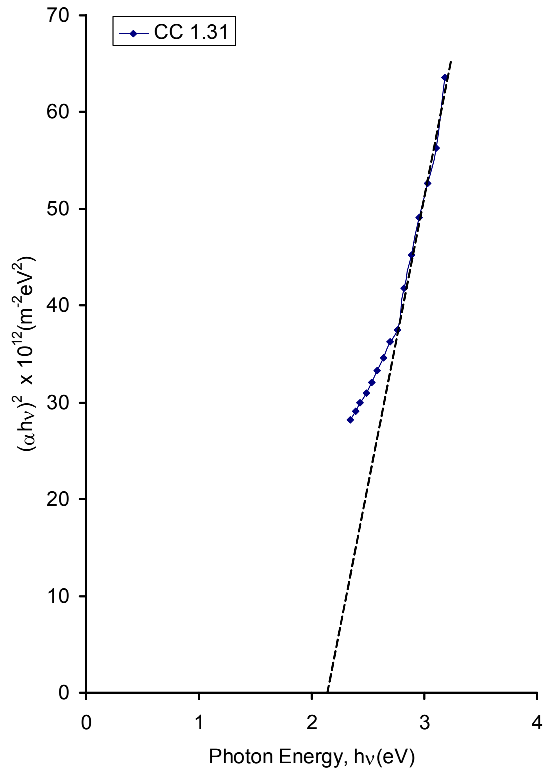

Fig.4 : Plot of $(\alpha h\nu)^2$ against Photon Energy for CuCl Sample Prepared at 300K.

CONCLUSIONS

Binary CuCl thin films were successfully grown *ab initio* on substrate at 300 K using the electroless method. The as-grown films were characterized for elemental composition using the energy dispersive X-ray fluorescence (EDXRF) and colorimetric method. The optical constants (index of refraction n, extinction coefficient k, and absorption coefficient a) were determined using the absorption (A), the transmission (T), and the reflection (R), at normal incident of light in the wavelength range of 200-850 nm The film has fairly high absorption in the UV region but very high absorption in the VIS region of about 400 – 700 nm. The high absorbance of the film made good materials for large area selective coatings for photothermal conversion of solar energy. The average index of refraction is 2.07 and average extinction coefficient of 7.81×10^{-2}. The index of refraction of $n > 2.0$ makes the material a good candidate for protective coatings. The plot of $(\alpha h \nu)^2 = f(h \nu)$ showed that the material is a direct band gap material with a band gap of about 2.20 eV. It could also be used in selective coatings for photothermal conversion of solar energy due to their high absorbance and for protective coatings

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