Growth and Optical Properties of $Cu_{1-x}Pb_xS$ Ternary Alloy Thin Films

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ABSTRACT

Group Ib – IV – VIa ternary alloy thin films of $Cu_{1-x}Pb_xS$ of about 0.89 nm thickness were prepared on glass substrates at 300 K using the solution growth method (SGM). The as-grown films were characterized for elemental composition using the energy dispersive X-ray fluorescence (EDXRF) and colorimetric method. The optical constants (i.e. index of refraction n, extinction coefficient k, and absorption coefficient α) were determined using the absorption (A), transmission (T), and reflection (R) at normal incident of light in the wavelength range of 200 – 850 nm. The compositional analysis shows that the film is rich in copper with mole factor x greater than 0.5 (x > 0.5). The average index of refraction (n) is 2.51. The index of refraction exhibited anomalous dispersion in the energy range of about 3.90 – 1.60 eV. The real and complex dielectric constants were found to be 6.32 and 0.21 respectively. A plot of $(\alpha hv)^2 = f(h\nu)$ shows that the film has a direct band gap (E_g) of about 2.60 eV.

(Key words: solution growth method, optical constants, optical band gap, E_g)

INTRODUCTION

Many ternary alloy materials have been prepared in thin film forms for photovoltaic, opto-electronic, and many other device applications. Many other techniques like evaporation, spray pyrolysis, sputtering, and others have been successfully employed for these purposes [6-7, 19]. The solution growth technique has been used to prepare ternary thin films of sulphides, selenides, and halides, which have tremendous applications in electronics, photonics, and photovoltaics. However, the material in this work is a new material and has not been deposited by the solution growth method. A close candidate, CuCdS, was prepared by depositing CdS on copper coated glass substrate [18].

The solution growth method has been used by many workers to prepare various thin films of sulphides, selenides, and halides [5-6, 8-9,14-16]. The aim of this work is to prepare thin films of $Cu_{1-x}Pb_xS$ by the convenient, conventional, and economic solution growth method, investigate their optical properties, compare the results with that of other methods in the literature, and determine their possible use in photovoltaics or in radiation detectors or emitters.

THEORY AND CALCULATIONS

Much of the information about the properties of materials is obtained when they interact with electromagnetic radiation. When a beam of light (photons) is incident on a material, the intensity is expressed by the Lambert-Beer-Bouguer law [4, 8]:

$$I = Io\ \exp\text{-}\alpha x\ ,$$

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 the absorption coefficient.

The absorbance (A) of the material is obtained directly by measurement and is given by [1, 8, 17]:

$$A = \log 1/T.$$

Hence, the transmittance is:

$$T = 1/10^A$$

Reflectance (R) is obtained from the relation:

$$A + T + R = 1.$$

The absorption coefficient (α) is the fractional decrease in intensity per unit increase in distance. That is,

$$\alpha = - dI/I_o.1/x$$

For a unit length, α is given by:

$$\alpha = \ln (1/T) = \ln (I_o/I)$$

The absorption coefficient is related to other optical properties as follows [10, 17, 19-21]:

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

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 [19].

The optical conductivity (σ) is related to absorption coefficient (α) by [8, 17]:

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

Thus the optical conductivity (σ) is:

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

The optical conductivity (σ) can easily be computed if α and n are known. The extinction coefficient (k) is related to complex index of refraction by [17]:

$$n_c = n\text{-}ik,$$

where n is the real part of the index of refraction and k is the complex part of the index of refraction also called extinction coefficient.

The complex dielectric constant (εc) is given by [8, 17]:

$$\varepsilon_c = (\varepsilon_1\text{-}i\varepsilon_{2)} = n_c^2 = (n + ik)^2$$

From which are derived:

$$\varepsilon_1 = n^2 - k^2$$

and,

$$\varepsilon_2 = 2nk.$$

For certain materials (insulators and semiconductors) where $k^2 << n^2$, the real dielectric constant is given by [9]:

$$\varepsilon_1 = n^2.$$

By the plot of $(n^2\text{-}1)^{-1}$ verses λ^{-2}, one can also obtain the complex dielectric constant from the point of intersection of the linear parts with ordinate [19].

At optical frequency (σ) tends to zero and n tends to $(\varepsilon)^{-0.5}$

Close to the absorption edge the absorption coefficient (α) is given by [6, 17, 20]:

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

where hν is the energy of the photon, Eg is the band gap, and 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 1/2 for all allowed indirect transitions to excitation states.

The plot of α^2 against hυ was used to obtain the band gap of the material (Figure 3.). The linear portion was extrapolated to the point where α = 0, giving, hυ = Eg. One can also plot a graphical representation of (αhν) = A $(h\nu - E_g)^{\gamma}$, were A is a constant [19].

EXPERIMENTAL METHODS

The starting materials used in the preparation of $Cu_{1-x}Pb_xS$ includes cadmium chloride ($CdCl_2.5H_2O$), lead chloride (PbCl2), copper sulphate (CuSO4.5H2O), thiourea $(NH_2)_2CS$ (MERK), EDTA (GPR), ammonia (NH_3), triethanolamine, TEA (BDH), and distilled water. The lead chloride ($PbCl_2$), was the source of cation (Pb^{2+}), copper sulphate, $CuSO_4.5H_2O$, was the source of another cation (Cu^{2+}), thiourea $(NH_2)_2CS$, was the source of anion (S^{2-}), while EDTA and TEA and were used complexing agents to slow down the reactions in order to eliminate spontaneous precipitation which is not healthy for the growth. NH_3 was used to provide an alkaline medium needed for the maximal growth. Various molar and volume concentrations of the starting chemicals were prepared using the distilled water and kept in well-labeled bottles and flasks as stock solutions. They were measured out appropriately into sets of thoroughly washed 50ml beakers and stirred vigorously with a glass rod.

The substrates, optically flat glass, were cleaned thoroughly by soaking in aqua-regia (a mixture of HCl and HNO_3 in 3:1 ratio) for about twenty-four hours (24h) to remove any grease, washed with detergent rinsed in water and dried in air. The substrates were immersed vertically and allowed to stand for various dip times. The growth parameters such as molar and volume concentrations, pH and time were altered in order to stabilize and optimize the growth. After some predetermined time, the substrates were removed from the chemical-baths, rinsed with distilled water, well labeled, and dried in air.

The reaction for the growth is represented as follows [8]:

$PbCl_2 + NH_3 \longleftrightarrow Pb(NH_3)^{2+} + 2Cl^-$

$Pb[NH_3]^{2+} \longleftrightarrow Pb^{2+} + NH_3$

$(NH_2)_2CS + OH^- \longleftrightarrow CH_2N_2 + H_2O + HS^-$

$HS^- + OH^- \longleftrightarrow S^{2-} + H2O$

$Pb(NH_3)^{2+} + (NH_2)_2CS + OH^- \longleftrightarrow PbS + NH_3 + (NH_2)_2CO$

$CuSO_4.5H_2O + TEA \longleftrightarrow [Cu(TEA)]^{2+} + SO4^{2-}$

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

Generally, the reaction is:

$Pb^{2+} + Cu^{2+} + S^{2-} \longleftrightarrow CuPbS$

The prepared films were optically characterized for optical constants using a double beam spectrophotometer (PYE UNICM 8-100, $\nabla\lambda \pm$ 0.1nm) in the range of 260-850 nm. The absorbance A was directly measured while the transmittance T, and reflectance R, and other optical constants (absorption coefficient a, extinction coefficient k, and index of refraction n) as well as the film thickness were obtained by computations [8-9,19].

RESULTS AND DISCUSSION

The as-grown films are brown in color and have good adhesion to the substrates. The elemental analysis performed with XRF and colorimetric methods showed that the material is a ternary alloy, $Cu_xPb_{1-x}S$, and is rich in lead with a mole fraction x > 0.5. Figure 1 shows the transmittance-reflectance spectra of the as-grown films at 300 K. The transmittance spectrum showed a maximum value of about 40% in wavelength range of 700- 800 nm and a minimum of about 21% in the wavelength of about 380 nm. The percentage transmittance is not very high. However, the transmittance property throughout UV/VIS/NIR makes the film a good material for thermal control window coatings for cold climates and antireflection coatings [8].

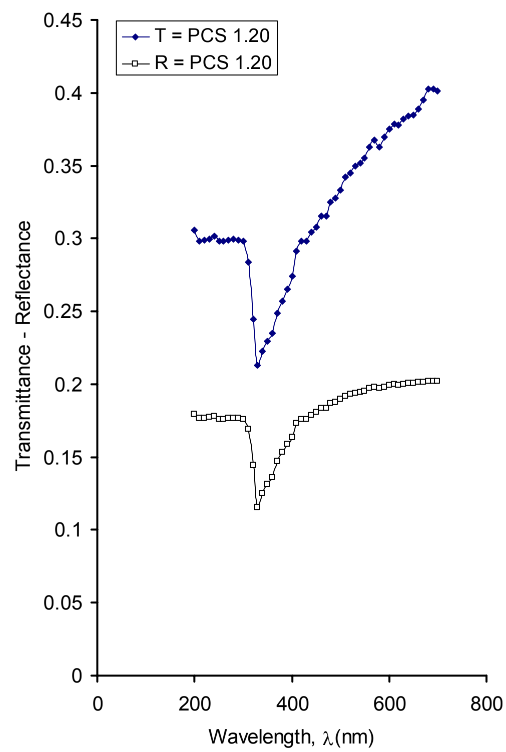

Fig. 1: Transmittance - Reflectance Spectra of CuPbS Film prepared at 300K.

The reflectance has a peak of about 18% corresponding to a wavelength of 380nm. The material is not a good reflector as the percentage reflectance is low.

The plot of $(\alpha h\nu)^2 = f(h\nu)$ (Figure 2) shows that the film has a direct optical band gap of about 2.50 eV. This value is higher than 2.40 eV band gap of the as-grown layers and the minimum of 2.28 eV around 280 C of thermal treatment (TT) obtained by Lozada-Morales, et al, [12] for cubic CdS thin films. This confirms the fact that the material is not CdS.

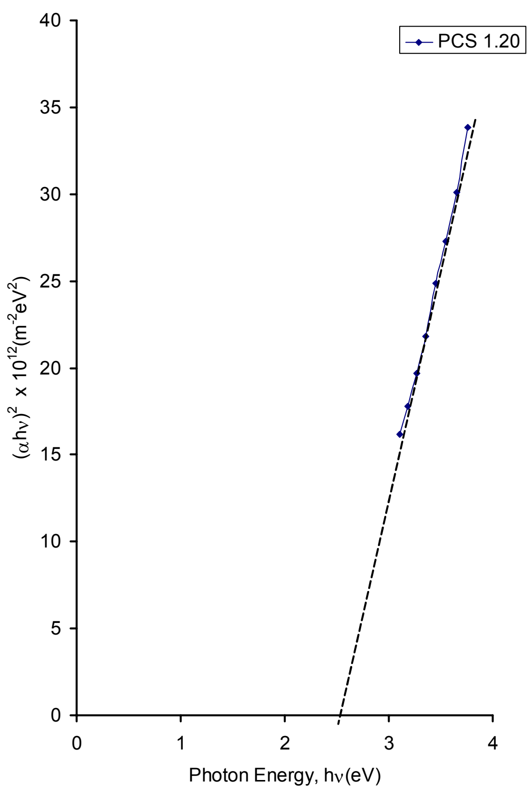

Fig.2: Plot of $(\alpha h\nu)^2$ against Photon Energy for CuPbS Sample.

The band gap of 2.50 eV suggests that the material is a semiconducting thin film, which could serve as a heterojunction in solar cell. The thickness of the films ranged from 0.39-0.84 microns. The mean optical conductivity of the material is 6.23×10^{14} s^{-1}. The material has high optical conductivity and hence, high electrical and thermal conductivities.

Figure 3 is a plot of the index of refraction (n) and extinction coefficient (k) with photon energy. The plot of n versus $h\nu$ is the dispersion curve for the material. The index of refraction has a step from 6.20 eV to about 3.90 eV, and then decreases with a decrease in $h\nu$ coming to a minimum of about 2.00, and then increases exponentially with a decrease in photon energy

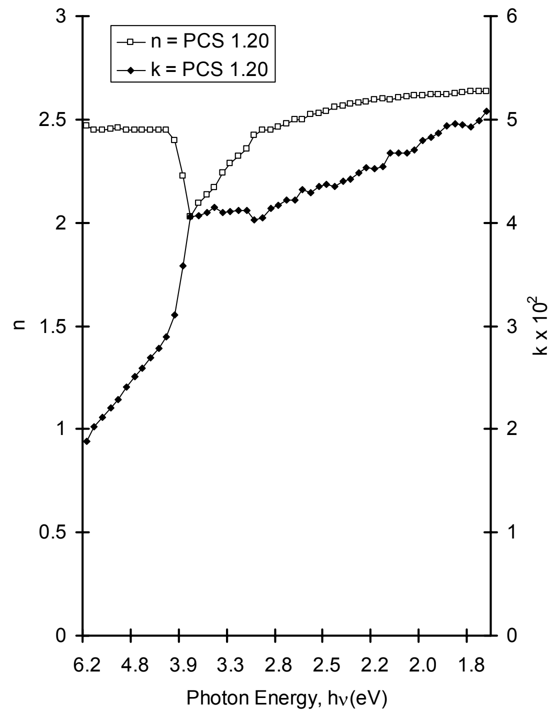

Fig.3: Plots of Refractive Index n and Extinction Coefficient k against Photon Energy for CuPbS Film prepared at 300K.

until it almost becomes constant at a value of about 2.50. It shows anomalous dispersion from the photon energy of 3.80 eV [11]. The mean value of the index of refraction is 2.51. The material has low optical transparency (n > 2.0) and could be used in antidazzling applications or in coatings for eyeglasses, TVs, and computer screens.

The extinction coefficient (k) increased with a decrease in photon energy, formed almost a step in the range 3.90-2.70 eV, and reached a peak of 5.20×10^{-2} at photon energy of about 1.60 eV

Figure 4 shows a plot of real dielectric constant ($\varepsilon 1$) and complex dielectric constant ($\varepsilon 2$) versus wavelength. The real dielectric constant showed peak and almost constant value of about 6.00 at the photon energy of about 6.20-3.80 eV and then increased exponentially with a decrease in photon energy to almost a constant value of 6.50. The complex dielectric constant ($\varepsilon 2$) increased linearly with a decrease in photon energy to a maximum value of 0.27 at the photon energy of about 1.40 eV. The mean value of the real dielectric constant is 6.33. The fairly high value of $\varepsilon 1$ suggests that the material could find applications in microelectronics for multiplayer capacitors [3].

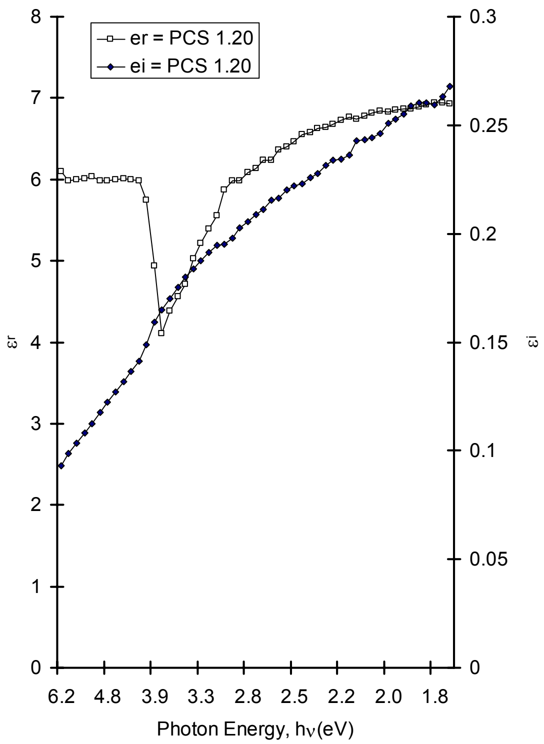

Fig.4: Plots of Real Dielectric Constant ε_r and Imaginary Dielectric Constant ε_i against Photon Energy for CuPbS Film.

CONCLUSIONS

Solution-grown ternary alloy $Cu_{1-x}Pb_xS$ thin films were successfully prepared and optimized on glass substrates at 300 K. Optical studies done to obtain the optical properties revealed that the film is a semi-conducting thin film with a direct band gap of 2.50 eV. The optimum index of refraction for the material is 2.51 corresponding to photon energy of about 1.40 eV. Optical studies reveal an interesting new area of application: the material has low optical transparency (n > 2.0) and could be used in antidazzling, coating of eyeglasses, TVs, and computer screens. The high transmittance property throughout UV/VIS/NIR makes the film a good material for thermal control window coatings for cold climates and antireflection coatings. Also, the fairly high value of $\varepsilon 1$ suggests that the material could find applications in microelectronics for multiplayer capacitors [3].

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