

# Optical Properties of Chemical Bath Deposited CuAlS<sub>2</sub> Thin Films

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## ABSTRACT

CuAlS<sub>2</sub> thin films were deposited on glass slides at room temperature (300K) from aqueous solutions of CuSO<sub>4</sub>·5H<sub>2</sub>O, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O, (NH<sub>2</sub>)<sub>2</sub>SC, in which triethanol amine (TEA) and ammonia solution were employed as a complexing agent and pH adjuster, respectively. The films were studied for their optical properties using Unicam® (UV-VIS spectrometry), model number UVG 065206.

The optical characterization shows that the band gap energy of the film is at 3.60eV. The film also exhibits peak transmittance of 27% in the ultra-violet region of the electromagnetic spectrum, and high absorbance of over 90% in the same region. The average refractive index (n) is between 2.00-2.54 with a peak extinction coefficient (k) of 6.65 x 10<sup>-2</sup> and optical conductivity values of 3.85 x 10<sup>13</sup>S<sup>-1</sup> to 6.80 x 10<sup>13</sup>S<sup>-1</sup>. The films show a low reflectance range of -2.1%-21% in near ultra-violet region of electromagnetic spectrum. Hence, CuAlS<sub>2</sub> could serve as good material for opto-electronic and photo-thermal applications.

(Key words: solar coating, thin film deposition, chemical deposition, optical properties, solid state characteristics, photovoltaic, copper aluminium sulphide).

## INTRODUCTION

Chalcopyrite semiconductor, copper aluminium sulphide (CuAlS<sub>2</sub>), is a promising material for opto-electronic device applications such as electroluminescent devices and photovoltaic cells. In opto-electronics, it can be used as a light emitting diode for various electronic applications because of its wide band gap energy (3.60eV at room temperature). In the area of optics, CuAlS<sub>2</sub> can be used as a selective window coating because of its high absorption coefficient in the ultraviolet region of

electromagnetic spectrum. Several techniques such as low-pressure metal organic vapor phase epitaxy (LPMOVE)<sup>1</sup>, Successive Ionic Layer Adsorption and Reaction (SILAR) method<sup>2</sup>; Pulsed Laser Deposition (PLD) method<sup>3</sup>; Traveling-Heater Method (THM)<sup>4</sup>; Molecular Beam Epitaxy (MBE)<sup>5</sup>; Low Pressure Metal Organic Chemical Vapor Deposition (LPMOCVD)<sup>6</sup>; and RF Diode Sputtering (RDS)<sup>7</sup> are some of the methods used to produce chalcopyrite semiconductor compounds.

In this paper, we report on the Chemical Bath Deposition (CBD) technique for the preparation of copper aluminium sulphide thin films which is a chalcopyrite semiconductor compound. This is a promising technique because of its simplicity; with this method a large area of thin film can be deposited without sophisticated instruments. The basic principle is that in order to precipitate a certain compound from a solution its ionic product (I.P) must exceed the solubility product (S.P).<sup>8</sup> And when this condition is satisfied the thin film of a particular compound is formed on the substrate by an ion-by-ion condensation process. In addition, an appropriate complexing agent is always involved to eliminate spontaneous precipitation. The essence of the complexing agent is to slow down the release of the metal ions on dissociation thus resulting in slow precipitation of the compound in the chemical bath by ion-ion reaction. The compound can form on the substrate as well as on the sides of the chemical bath as thin films by this method. For a typical metal (M) and complexing agent (A), the existence of free metal ions in the solution can be explained by the equilibrium reaction.



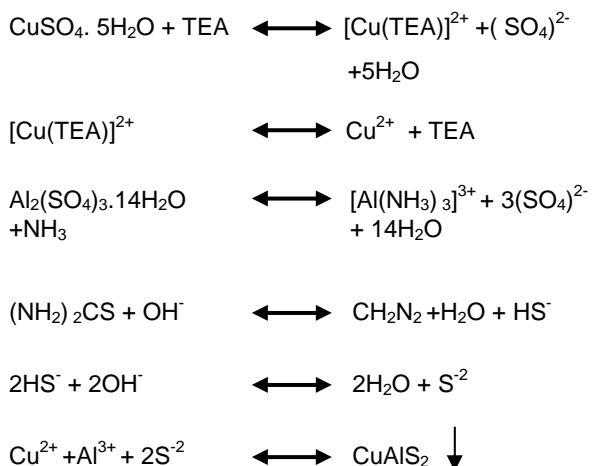
The deposition rate is controlled by the concentration of metal ions present in the solution and this is achieved by controlling the concentration and temperature of an appropriate complexing agent.

## EXPERIMENTAL DETAIL

The substrate used for the deposition of CuAlS<sub>2</sub> thin films were commercial microscope glass slides. Before deposition, the substrates were degreased with HCL, washed with detergent and dried in air. The importance of degreasing is to remove any remaining dirt and to ensure clean surfaces.

Aqueous solutions of 0.12M CuSO<sub>4</sub>.5H<sub>2</sub>O, 1.0M thiourea [(NH<sub>2</sub>)<sub>2</sub>SC], 0.08M Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.14H<sub>2</sub>O, 7.4M of TEA and pH adjuster ammonia (NH<sub>3</sub>) were used to prepare CuAlS<sub>2</sub> thin films. First, 5ml of CuSO<sub>4</sub>.5H<sub>2</sub>O was put in a 50ml beaker and this was followed with the addition of 5ml of TEA. The resulting solution was stirred for few minutes until the solution becomes bluish and homogenous. 5ml of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was later added and the solution was also stirred before addition of 5ml of ammonia and 5ml of thiourea respectively. A dark orange black solution was formed and deionised water was finally added making up the volume to a total of 50ml.

Several baths were prepared in this way and left to stand for 24 hours, after which the slides were removed, rinsed in distilled water, and dried in open air at room temperature (300k). For optical absorption and transmittance measurement of the films deposited on glass slides, a similar blank slide was used as reference frame in the Unicam<sup>®</sup> UVG065206 spectrophotometer. The stepwise reactions involved in the complex ion formation and film deposition processes for CuAlS<sub>2</sub> are hereunder stated.



Sulphide ions are released by the hydrolysis of thiourea and Cu<sup>2+</sup> and Al<sup>3+</sup> ions form cuprous triethanolamine and tri-ammonium aluminate complex ions respectively by combining with TEA and NH<sub>3</sub> in the pH range of 8 and 9. The [Cu(TEA)]<sup>2+</sup> and [Al(NH<sub>3</sub>)<sub>3</sub>]<sup>3+</sup> complexes which combine with S<sup>2-</sup> ions to form dark green or black CuAlS<sub>2</sub> thin film on the glass slide.

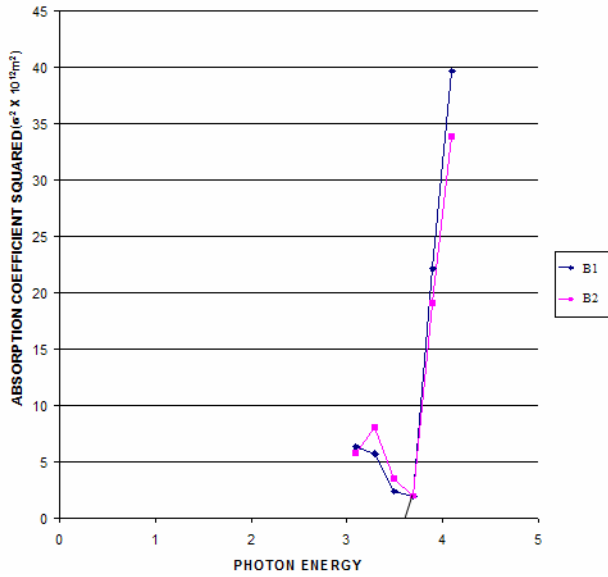
The optical properties of CuAlS<sub>2</sub> thin films were determined from transmission and absorbance measurement in the range of 200 – 1000nm carried out on the films.

Figure 1 shows the determination of optical band gap energy of CuAlS<sub>2</sub> thin films, which was found to be at 3.60eV. This is just the intercept of the straight part of the plot of absorption coefficient squared against photon energy. This shows that CuAlS<sub>2</sub> is a direct wide band gap energy semiconductor material.

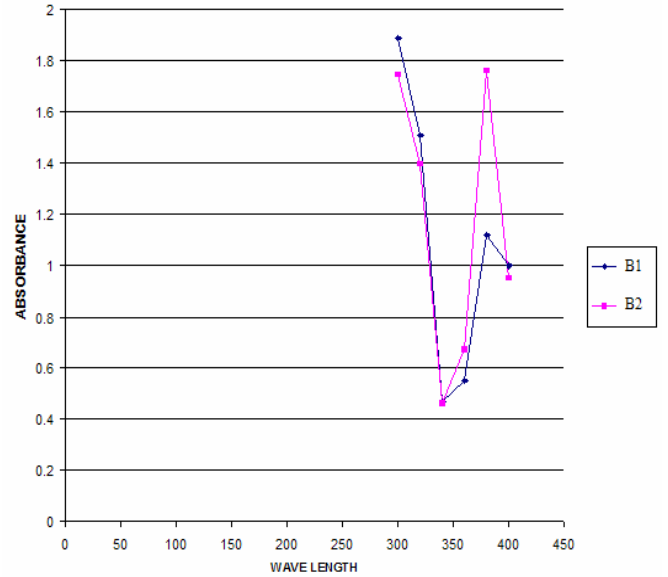
Figure 2 is a plot of transmittance against wavelength in the UV region for samples B1 and B2. Sample B1 was obtained at the pH value of 8.95 and B2 at the pH value of 9.51. The result shows a peak optical transmittance of 27% at wavelength of 340nm. The extrapolation of the graph shows zero transmittance at 250-300nm. This property of poor transmittance in the UV region makes the film a good material for screening off the UV portion of the electromagnetic spectrum which is dangerous to human health.

Figure 3 is the plot of absorbance against wavelength in the UV region for samples B1 and B2. It shows a high absorption coefficient of the films in the UV-region (250-300nm). This confirms the ultraviolet photoluminescence (PL) studies carried out on CuAlS<sub>2</sub> heteroepitaxial layers grown by PLMOCVD technique by Chichibu, Nakanish, and Shirakata<sup>6</sup>. This makes the film a good candidate for selective window coatings for photovoltaic applications.

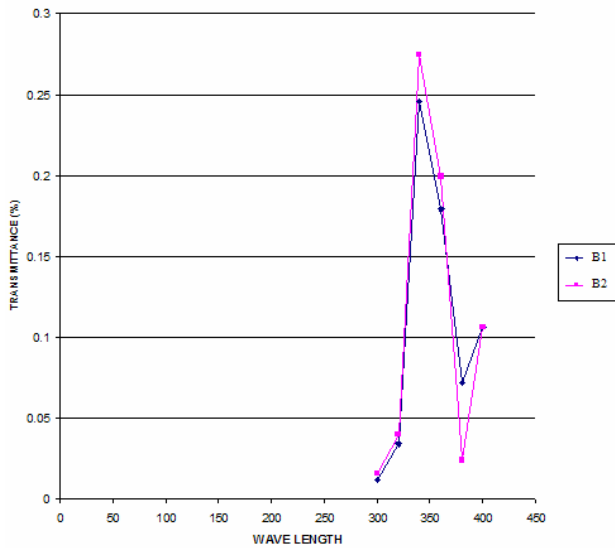
In addition, Figure 4 shows the graph of refractive index (n) of the films against the photon energy in the visible region for samples B1, B2, and B3. Sample B3 was obtained at pH value of 8.63. It exhibits cluster around 2.00-2.54 showing that the average value falls within this range.



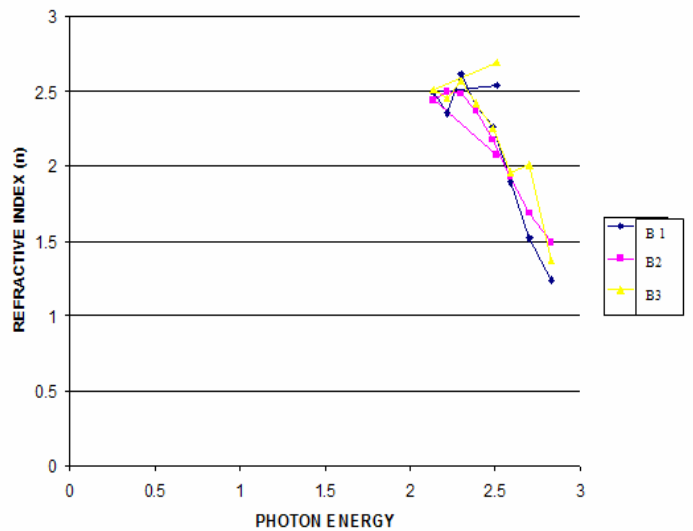
**Figure 1:** Plot of Absorption Coefficient Squared against Photon Energy.



**Figure 3:** Plot of Absorbance against Wave Length in the UV Region for Samples B1 and B2.



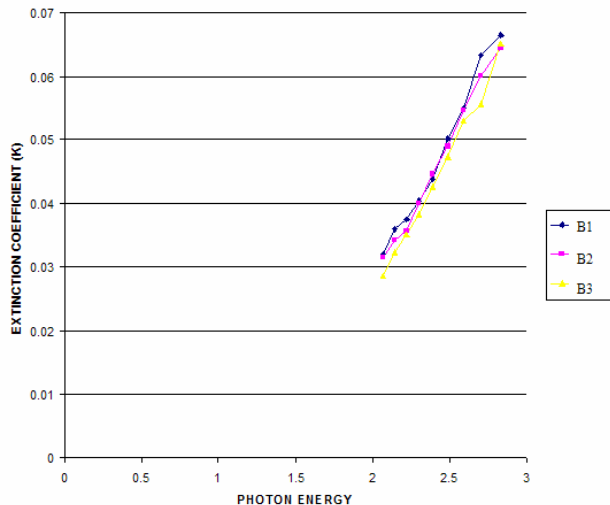
**Figure 2:** Plot of Transmittance versus Wave Length in the UV Region for Samples B1 and B2.



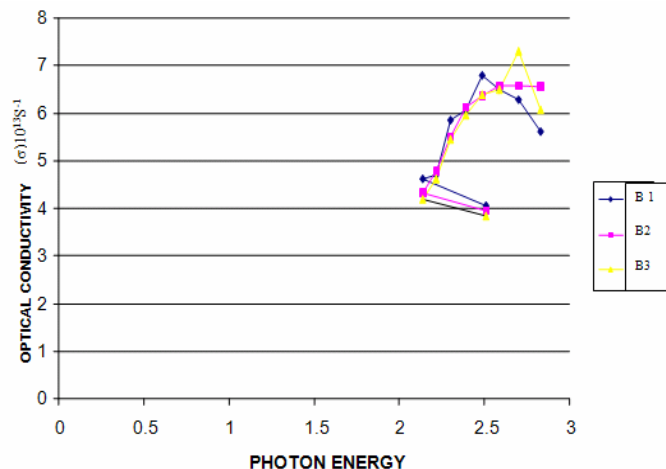
**Figure 4:** Refractive Index versus Photon Energy in the Vis-Region for Samples B1, B2, and B3.

The variation of extinction coefficient ( $k$ ) with photon energy for samples B1, B2, and B3 is shown in Figure 5. The maximum extinction coefficient ( $k$ ) value occurs at  $6.65 \times 10^{-2}$  at photon energy of 2.83 eV and at pH value of

8.95. This shows that the extinction coefficient increases as the frequencies of solar radiation increases.



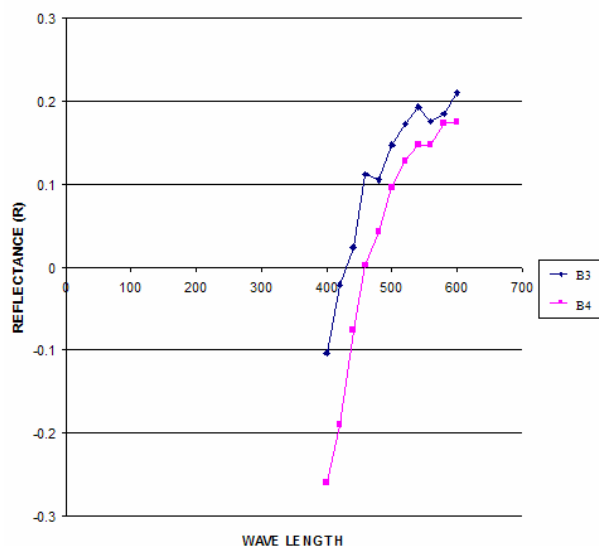
**Figure 5:** Plot of Extinction Coefficient against Photon Energy for Samples B1, B2, and B3.



**Figure 6:** Plot of Optical Conductivity against Photon Energy for Samples B1, B2, and B3.

A plot of optical conductivity ( $\sigma_{op}$ ) against photon energy is portrayed in Figure 6 for samples B1, B2, and B3. The value ranges from  $3.85 \times 10^{13} \text{S}^{-1}$  to  $6.80 \times 10^{13} \text{S}^{-1}$  with the peak value at  $6.80 \times 10^{13} \text{S}^{-1}$  for photon energy value of 2.49eV.

Figure 7 is the variation of reflectance with the wavelength of incident radiations in the visible region for samples B3 and B4. Sample B4 was deposited at the pH value of 8.48. The plot reveals very low or zero reflectance at near ultraviolet region of electromagnetic spectrum. The figure further indicates that reflectance increases towards the visible region and infra-red region of electromagnetic spectrum.



**Figure 7:** Plot of Reflectance against Wave Length in the Vis Region for Samples B3 and B4.

## CONCLUSION

Thin films of  $\text{CuAlS}_2$  have been deposited by Chemical Bath Deposition (CBD) method on commercial glass substrate. The transmittance and absorbance measurement carried out on the films show that the films has high absorption coefficient, and poor transmittance and reflectance values in the UV region of electromagnetic spectrum. The film has wide band gap energy of 3.60eV and refractive indexes of average range of 2.00-2.54. Also, with peak extinction coefficient value of  $6.65 \times 10^{-2}$  and optical conductivity range between  $3.83 \times 10^{13} \text{S}^{-1}$  and  $6.80 \times 10^{13} \text{S}^{-1}$ . Consequently, the films could be used in the fabrication of window

layers for photocells, and for construction of light emitting devices because of its opto-electronic characteristics.

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## SUGGESTED CITATION

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