

# Influence Of Substrate Temperature on Optical Properties of Nanostructured CuAlS<sub>2</sub> Thin Films Grown By Two Stage Vacuum Thermal Evaporation Technique

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**Abstract:** CuAlS<sub>2</sub> thin films were prepared by two stage thermal vacuum evaporation technique. The substrate temperature was varied in the range 300-473K and seems to be one of the most important parameters affecting the physical properties of the films. The optical constants of the deposited films were obtained from the analysis of the experimental recorded transmission spectral data over the wavelength range 200 –1100 nm. The entire optical constants were found to be dependent on substrate temperature. The values of some important parameters of the studied films are determined from these spectra. The low value of the extinction coefficient as observed in our films is a qualitative indication of excellent surface smoothness of the films. An analysis of the optical absorption data of deposited films revealed an optical direct transition with the estimation of the corresponding band gap values. A slight increase in the direct optical gap from 1.95 eV to 1.77 eV as the substrate increases from 300 to 473 K was observed.

**Keywords:** Thermal evaporation, Substrate temperature, Sulfurisation temperature, Optical parameters

## I. INTRODUCTION

The ternary compound CuAlS<sub>2</sub> belongs to the I-III-VI family of semiconductors with chalcopyrite type structure. Chalcopyrite semiconductor, copper aluminum sulphide (CuAlS<sub>2</sub>), is a promising material for its technological 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 3.50eV at room temperature [1], the widest value among other chalcopyrite compounds make it suitable material for use in wide band gap photovoltaic cell (WBGp) as well as in photovoltaic optical detectors. 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. The good luminescent properties and high absorption coefficient make it a good candidate for use as light emitting diode LED [2]. Several techniques such as Chemical bath deposition [1], [2], Metal decomposition [3] e.t.c have been used to prepare this semiconductor material. In this work we reported the influence of substrate temperature on CuAlS<sub>2</sub> thin films prepared by two stage vacuum thermal evaporation techniques.

## II. MATERIALS AND METHOD

### 2.1 Materials

All the chemicals used (copper, aluminum and sulfur) for the deposition of CuAlS<sub>2</sub> thin films were 4N grade. Corning 7059 glass was used as substrate. Deposition of Cu-Al alloys was performed by using EDWARDS FL 400 thermal evaporator which was equipped with SQC 310 Deposition controller. A molybdenum boat was used to evaporate Cu thin films and tungsten coils was used for deposition of aluminum placed at a distance of 10cm from the glass substrate. The substrate temperatures were room temperature (RT), 373K and 473K. Cu-Al precursors were converted to CuAlS<sub>2</sub> thin films by sulfurisation using SVG 2610 BASE horizontal diffusion furnace. The sulfurisation was carried out at the temperature of 573K.

### 2.2 Film Preparation

#### 2.2.1 Substrate preparation

Corning 7059 glass was used as substrate in deposition of thin films. The cleaning process is employed since the cleanliness of substrate has an important effect on deposition of high quality thin films. It involves following several stages to remove the contaminations such as organic contaminants, oil and protein molecules which may appear on glass surfaces on to which the film is being deposited.

- (a) To clean oils and protein molecules substrates were kept in dilute chemical detergent at a temperature of 100°C in ultrasonic bath for 10 minutes, and rinsed with hot distilled water to remove the possible left detergent contaminants.

- (b) To remove organic contaminants substrates were immersed in a boiling diluted H<sub>2</sub>O<sub>2</sub> solution for nearly 15 minutes; the same solution were put into ultrasonic cleaner for 15 minutes, substrate extracted from this solution were then rinsed with hot distilled water and kept in methanol to be ready for use.
- (c) To use the substrate for deposition process, the substrates taken from the methanol were dried by blowing pressuring N<sub>2</sub> gas.

### 2.2.2 Growth of CuAlS<sub>2</sub> Thin Films

CuAlS<sub>2</sub> thin films were prepared by two stages:

- (a) Sequential deposition of Cu and Al layers on glass substrate to form Cu-Al precursor.
- (b) Sulfurisation of this precursor to convert it to CuAlS<sub>2</sub>

#### 2.2.2.1 Sequential Deposition of Cu-Al Precursor

The deposition of Cu-Al alloy was carried out by using an **EDWARDS FL 400** thermal evaporator. A metallic precursor with Cu-Al bi-layer structure was prepared on glass substrate by vacuum thermal evaporation of 4N grade copper and aluminum in a sequential mode. Molybdenum boat was used as source for the deposition of copper and tungsten coils was used for deposition of aluminum.

#### 2.2.2.2 Sulfurisation/annealing of CuAl thin films

Sulfurisation is the conversion of metallic Cu-Al thin films to CuAlS<sub>2</sub> thin films by reaction in sulfur vapor at a given temperature. In this work sulfurisation process of the Cu-Al thin films grown was carried out in a horizontal diffusion furnace (**SVG STSTEM 2610 BASE**) at a temperature of 573K.

Prior to sulfurisation samples were inserted into the sulfurisation chamber of the furnace using a long Pyrex cylinder. Nitrogen gas was then passed into the furnace for 30 minutes to flush out the air which might be trapped in the furnace chamber. The heat of sulfur furnace containing elemental sulfur was raised to a temperature of 413K, above melting point of sulfur (386K) and the diffusion furnace heat was raised to the temperature of 573K at a ramp rate of 10<sup>0</sup>/min, the dwell period was set to one hour and when the two temperatures were attained the sulfur vapor was allowed to diffuse into the sample at the rate 4.3 standard cubic centimeter per minute Scm by using Argon as a carrier gas. The samples were kept at that temperature and after one hour the furnace started to cool down naturally and was switched off when its temperature reached 413K. The samples were withdrawn from the furnace cooled to a room temperature.

## 2.3 Theoretical considerations

### 2.3.1 Optical transmittance

The optical absorbance A was calculated from the relation [4]

$$A = \log \frac{1}{T} \quad (1)$$

T is the transmittance.

### 2.3.2 Determination of absorption coefficient $\alpha$

The absorption coefficient  $\alpha$  was calculated from the relation [5]

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{d} \quad (2)$$

Where T is transmittance and d is the film thickness

### 2.3.3 Photon energy E

The photon energy, E, is given by [4]

$$E = h\nu \quad (3)$$

Where h is the plank constant and  $\nu$  is the frequency of the photon.

Similarly,

$$E = \frac{hc}{\lambda} \quad (4)$$

Where c is the speed of light and  $\lambda$  is the wavelength. Substituting for constants in equation (4) gives:

$$E = \frac{12,400}{\lambda} eV \quad (5)$$

### 2.3.4 Energy band gap $E_g$

The optical band gap of the films is determined by applying the Tauc model

$$\alpha h\nu = A(h\nu - E_g)^n \quad (6)$$

Where  $E_g$  is the band gap corresponding to a particular transition occurring in the film,  $A$  is a constant,  $\nu$  is transition frequency and the exponent  $n$  characterizes the nature of the band transition. The relationship between  $(\alpha h\nu)^2$  and  $h\nu$  is plotted. The  $E_g$  value can be obtained by extrapolating the linear portion to the photon energy axis.

### 2.3.5 Extinction coefficient $k$

The extinction coefficient or total attenuation coefficient  $k$  was determined by employing the relation [4]

$$k = \frac{\alpha \lambda}{4\pi} \quad (7)$$

For which  $\lambda$  is the wavelength of light.

## III. RESULTS AND DISCUSSION

### 3.1 Transmittance

Fig. 3.1 shows transmittance spectra of the CuAlS<sub>2</sub> films obtained at room temperature (300K), 373K and 473K respectively and each sulfurised at 573K. It is observe that in all the films the transmittance decreases abruptly in the ultraviolet (UV) region, while in the visible (VIS) and infrared (IR) regions high transmittance was observed. The high transparency in the visible VIS and infrared IR regions is a consequence of the wide band gap of the film [6]. On the other hand the low transmittance in the UV region is an indication that at lower wavelengths there is no transmission because all the light is absorbed. For higher wavelengths region however there are no appropriate electronic transitions possible so transmission is very high in this range.

It can be seen from fig. 3.1 that for all the samples transmission is dependent on substrate temperature. Transparency increases with increase in substrate temperature. Similar observations were reported by [7], [8] and [9], which according to them the improved transmittance with escalating substrate temperatures enhances improvement in structural homogeneity and better crystallinity. Furthermore, at higher substrate temperatures the optical scattering diminishes and thus leads to enhancement of optical transmission. The transmission spectrum for films grown at room temperature (RT) in the visible wavelength region (400–700nm) is observed to be 33.5%. For films grown at 373K, optical transmission was found to increase to 38%. As substrate temperature is further increased to 473K it is observed that the transmittance increased to as high as 46%.

These values are improvement over those obtained by [1] and [2]. The higher transmittance of the material in the visible regions at high temperatures makes it a strong candidate for use in optoelectronic devices. These characteristics of high transmission in VIS and IR are applicable in photovoltaic industry or solar cell fabrication and also in photo-thermal application. Also, relative high transmittance of the films in the VIS and infrared (IR) region make the films suitable materials for eye glasses industry as they are capable of transmitting the visible radiation needed for vision. They are capable of transmitting the infrared radiation (IR), the heat radiation giving human beings and animals the necessary warmth

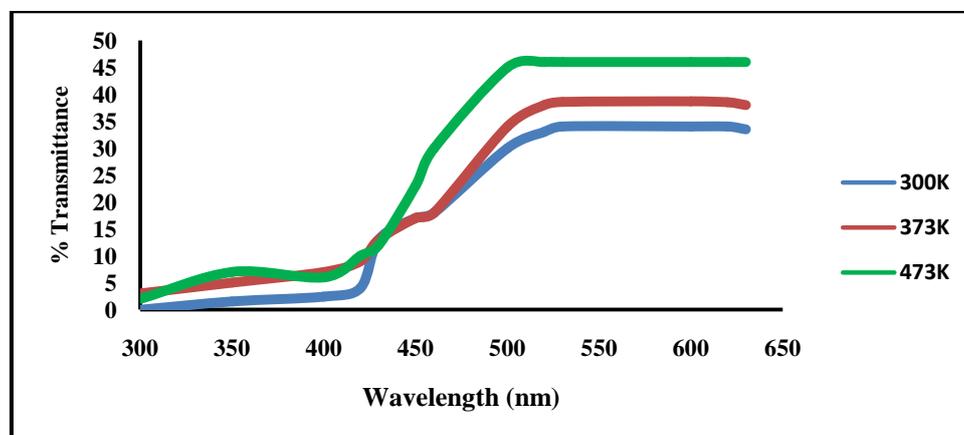


Figure 3.1 Transmission spectra for CuAlS<sub>2</sub> films at different substrate temperature

### 3.2 Absorbance

The variation of optical absorbance with wavelength for CuAlS<sub>2</sub> thin films grown at different substrate temperatures is displayed in fig. 3.2. In all cases it is observed that the absorption decrease with increase in substrate temperature. As can be seen from figure at 300K, 373K and 473K substrate temperatures the films exhibited an absorbance of 3.3, 3.0 and 2.5 respectively. This consequently implies an improvement in transmission of the films. The value of absorbance is also low in the VIS-IR regions and sometimes close to zero, however it is found to be high in ultra violet region. The enhanced absorption is observed in the neighborhood of  $\lambda = 300$  nm. This makes the film a good window layer for solar cell application. The low absorption of energy makes CuAlS<sub>2</sub> useful for optical components in high laser window and multispectral applications, providing good imaging characteristics.

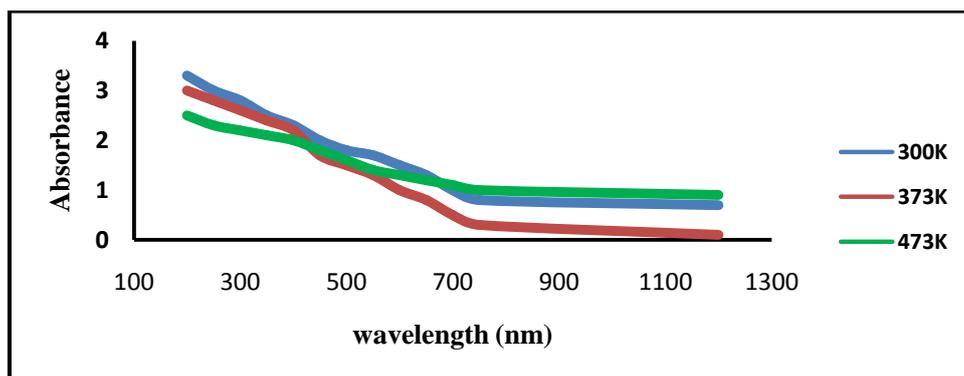


Figure 3.2 Absorbance vs. wavelength for CuAlS<sub>2</sub> films grown at different substrate temperature

### 3.3 Direct optical band gap energy

The plot of  $(\alpha hv)^2$  versus photon energy  $hv$  (wavelength range 200-1200 nm) in respect of CuAlS<sub>2</sub> films prepared at different substrate temperatures and sulfurised at 573K is illustrated in fig. 3.3. The plot is linear in the region of strong absorption near the fundamental absorption edge (i.e. presence of a single slope in the plot). Thus, this suggests that the films have direct and allowed transition. The values of the direct optical band gap  $E_g$  were determined by extrapolating the linear region of the plots to zero absorption ( $\alpha hv=0$ ).

The optical band gap was found to depend upon substrate temperature. Samples deposited at room temperature (300K) and sulfurised at 573K the energy band gap of 2.8eV was observed. When the substrate temperature was raised to 373K, the value of band gap increased to 3.05eV. In the same trend when the substrate temperature was further increased to 473K, the band gap energy attained a value of 3.2eV. These values closely agree with 3.0eV, and 3.2eV reported by [8] and [10] respectively, but lower than 3.6eV reported by [1]. The result showed that there is a shifting in band gap toward high energy which may be due to transformation to crystalline phase taking place at high substrate temperatures. In general, the increase in substrate temperatures give rise to the decrease in disorder and defect density in the structure which give rise to increase in the optical band gap. The band gap values exhibited by the films are ideal for photovoltaic application. Thus, this suggests that the optimized deposition temperatures are ideal for obtaining good chalcopyrite single phase CuAlS<sub>2</sub>

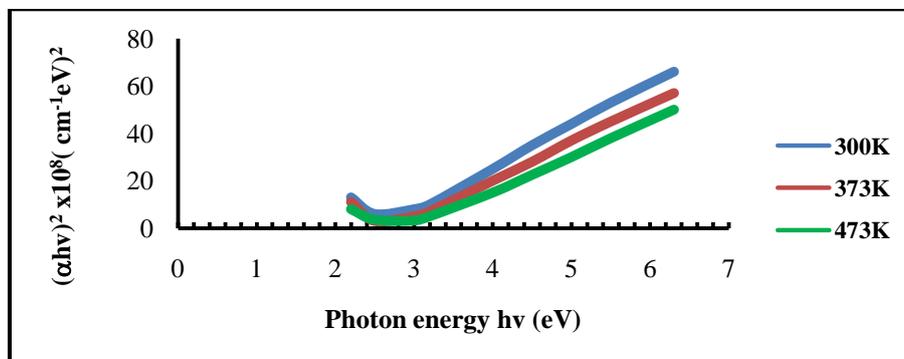


Figure 3.3  $(\alpha hv)^2$  vs. Photon energy for CuAlS<sub>2</sub> thin films at different substrate temperature

### 3.4 Extinction coefficient (k)

The results of dependence of extinction coefficient  $k$  on wavelength for CuAlS<sub>2</sub> thin films deposited at three different substrate temperatures and sulfurised at 573K temperatures is illustrated in fig. 3.4. It is observed in each case that the extinction coefficient  $k$  decreases with increasing substrate temperature, and wavelength. This behavior is a clear indication that films are becoming highly transparent at long wavelengths. Thus, this suggests that the increase in transparency is likely to be originating from the observed decrease in  $k$  with increasing substrate temperature in the same wavelength range.

The observed  $k$  in respect of the film prepared at room temperature is 0.36. As substrate temperature increases from room temperature to 373K a further decrease in  $k$  was exhibited by the films, in which  $k$  slashed to 0.29. By further elevating the substrate temperature to 473K, extinction coefficients as low as 0.27 was observed. These values of  $k$  are in good agreement with those obtained by [1] and [11]. The decrease of  $k$  with increasing substrate temperature may be due to the improvement in the crystallinity which leads to minimum imperfection.

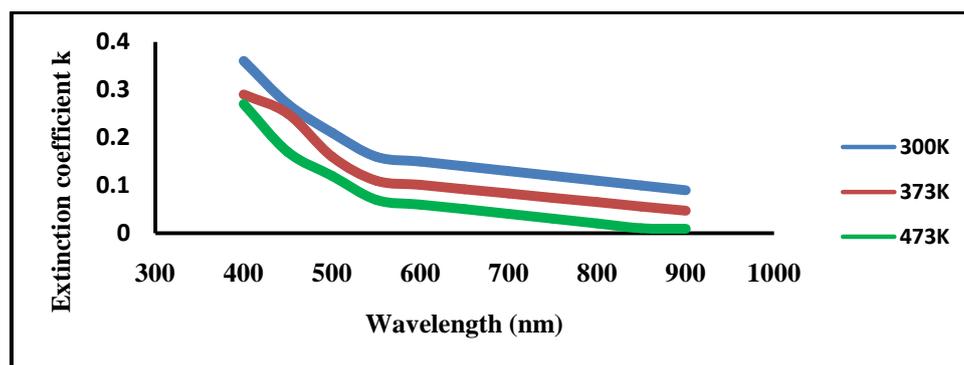


Figure 3.4 Extinction coefficient vs. wavelength for CuAlS<sub>2</sub> films at different Substrate temperature

#### IV CONCLUSION

Crystalline CuAlS<sub>2</sub> thin films have been prepared on glass substrate at different substrate temperature by two stage vacuum thermal evaporation technique. It was found that all the optical parameters are dependent on substrate temperature. Absorbance and extinction coefficient were found to decrease with increase in substrate temperature. However transmittance increases with increase in substrate temperature. An energy band gap of 3.25eV was obtained for films grown at an elevated substrate temperature. Thus, it may be concluded that CuAlS<sub>2</sub> thin films obtained in this work, are of good quality and would benefit the fabrication of photovoltaic devices such as window layers for solar cells, selective window coating and for construction of light emitting devices.

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