

TEMPERATURE-DRIVEN MODIFICATIONS IN CuAlSe_2 THIN FILMS SYNTHESIZED BY CHEMICAL BATH DEPOSITION

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DOI: <https://doi.org/10.5281/zenodo.17422760>

Abstract

A low cost chemical bath deposition technique has been used for the preparation of Copper aluminum diselenide (CuAlSe_2) compound thin films onto commercial microscope glass substrates at variation of deposition temperature. The effects of deposition temperature (above room temperature (27°C)) towards the optical properties of the films were investigated. The optical properties were investigated by Jenway software 6405 UV-Vis spectrophotometer. The optical band gap energy of the films above room temperature ranges from 2.00 – 2.14 eV depending on the deposition temperature.

Keywords: chemical bath deposition, CuAlSe_2 , deposition temperature, optical properties

Introduction

Copper aluminum chalcogenides semiconducting materials have been investigated at recent years as a potential material for realization blue LEDs, solar cells and other optoelectronic applications. In particular, the wide-gap compound CuAlSe_2 is considered potentially useful for photovoltaic solar cell application, and as thermal window glass coating material. There are many methods of preparing thin films, such as chemical bath deposition [1], Electrodeposition [6], Travelling heater [10], Potentiostatic deposition [9], MetalOrganic Vapour Phase epitaxy (MOVPE) [6], Low- pressure Metalorganic Chemical-Vapour deposition [3], Vacuum evaporation [4], Close Space chemical bath deposition [8].

In this paper, we prepared CuAlSe_2 thin films by chemical bath deposition technique and studied the effects of deposition temperature (above room temperature (27°C)) on the properties of this material. We report the chemical bath deposition of CuAlSe_2 thin films at variable temperature in an alkaline medium (pH = 8.86) at deposition time of 24 hours. The deposition parameter was optimized to obtain good quality thin films. The properties like absorbance, reflectance and transmittance with wavelength were analyzed under varying bath temperature (50°C – 70°C). The film thicknesses of the samples were analyzed with respect to the various deposition temperatures. The optical conductivities and the refractive index against photon energy were determined. The band gap energy was determined from the influence of the deposition temperature.

Experimental Preparation of Samples

All the reagents used for the deposition of CuAlSe_2 were analytical grade reagents and all the solutions were prepared using pure laboratory distilled water. The chemicals compounds used were copper chloride

($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Aluminum trisulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$), Sodium Selenosulphate (Na_2SeSO_4), Ethylenediaminetetraacetic acid disodium Salt [Na_2EDTA] ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot \text{H}_2\text{O}$) and Ammonia Solution (NH_3 Soln).

The Copper Chloride, Aluminum trisulphate and sodium selenosulphate acted as a source of copper, Aluminum and selenium ions respectively. The Na_2EDTA was used as a complexing agent to combine with Cu^{2+} and Al^{3+} to obtain Cu-EDTA and Al-EDTA complex solutions. NH_3 soln was used as a pH adjuster. The presence of Na_2EDTA was found to improve the lifetime of the deposition bath as well as the adhesion of the deposited films on the commercial microscope glass substrates. Before deposition, the substrates were degreased with HCl, followed by cleaned with distilled water and dried in open air. Deposition of CuAlSe_2 thin films were carried out by using the following procedure:

Firstly, 5ml of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1M) and 5ml of $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ (0.1M) solutions were complexed with 5ml of Na_2EDTA (0.1M), and stirred for several minutes to get clear and homogeneous solutions. Thereafter, 5ml of Na_2SeSO_4 and NH_3 solution (0.1M) were added under stirring conditions with respect to the variation of their deposition temperature. The clean commercial microscope glasses were then placed vertically inside the different beakers without disturbing them. The beakers were allowed to stand for 24 hours at alkaline medium. After deposition, the substrates were removed from the beakers and cleaned with distilled water. The deposited films were dried in an open air and subjected to further analyses.

Characterization Of Thin Films

The optical characterization recorded the optical absorbance and transmittance carried out with the aid of Jenway Software 6405UV-VIS spectrophotometer. The optical absorption measurement was carried out in the wavelength range from 300 to 700nm using the UV-Vis spectrophotometer. The film-coated substrate was placed across the sample radiation pathway while the uncoated substrate was put across the reference path.

Results and Discussion

Fig. 1 shows the optical thickness of CuAlSe_2 thin films in the wavelength region from 300 to 700 nm at respective deposition temperature of 50°C , 65°C and 70°C . As seen, the film thicknesses increase as the bath temperature increase.

Fig. 2 shows the optical absorption spectrum of the compound thin films, which shows high absorption in the visible range of 420nm to 680nm indicating that these materials can be used for photovoltaic solar cell applications. The graphs show the increasing order of absorbance of samples as 20, 19 and 16 which has deposition temperature of 70°C , 65°C , and 50°C respectively. This shows that at minimum temperature of 50°C , highest absorbance of visible radiation occurred.

The graph of transmittance versus wavelength in fig. 3 shows that it is only sample 16 has low transmittance in general while others have high transmittance at UV region. Sample 19 has highest transmittance. This shows that it can be used for thermal window glass coating.

In fig. 4, the reflectance at the wavelength range of 380nm to 480nm for all samples is high. It shows that as the deposition temperature increases, the reflectance also increases. Sample 20 (70°C) has the highest reflectance value.

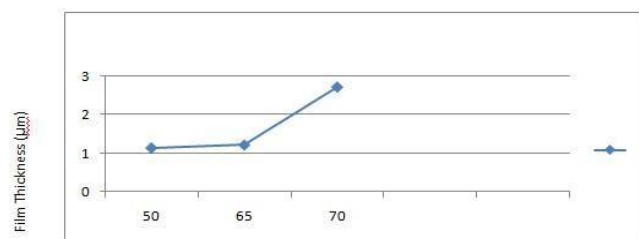
Fig. 5 equally shows the plot of optical conductivities versus photon energy. The optical conductivities of each sample increases linearly with the photon energy. Sample 16 (50°C) has the highest optical conductivity while sample 20 (70°C) has the least optical conductivity. It shows that samples with highest optical band gap energy will trap more energy from the sun. Therefore, it is expected to grow films below and at room temperature to enhance their conductivities.

Also figure 6 shows the plot of refractive index versus photon energy and we were able to see that each sample exhibited the same behavior at all photon energy levels. Sample 20 has highest refractive index value. This behavior shows that the compound thin films can be used in coating glasses since they have high refractive index values.

CuAlSe₂ being a direct band gap semiconductor, the absorption coefficient in the region of strong absorption obeying the equation:

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

Where α is the absorption coefficient, h is the Planck constant, ν is the radiation frequency, E_g is the band gap energy and A is a constant which depends on the nature of the radiation. The linear nature of the plot indicates the existence of direct transition [4]. The band gap values found at variation of deposition temperature within the range of values 2.00 to 2.14 eV as in figure 7a - c. The band gap energy decreases as the bath temperature increases.



Bath temperature (°C)

Fig. 1: A graph of film thickness versus the deposition temperature for samples 16, 19, and 20

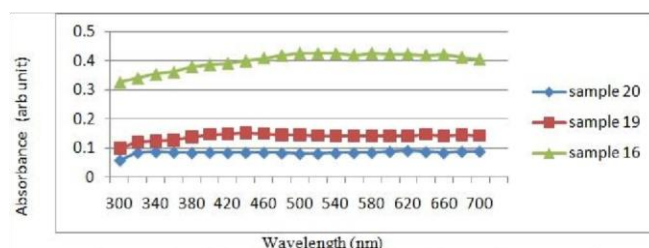


Fig. 2: Graphs of absorbance versus wavelength for samples 16, 19 and 20

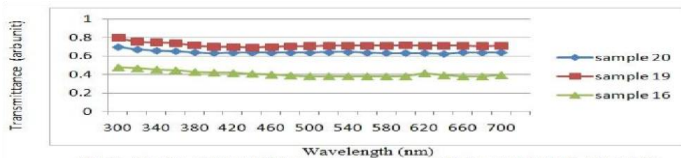


Fig. 3: Graphs of transmittance versus wavelength for samples 16, 19 and 20

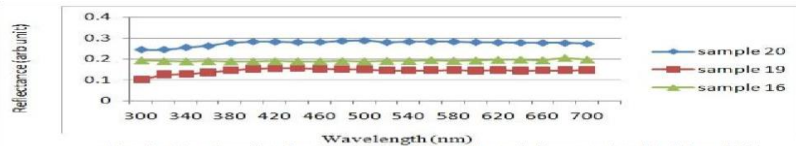


Fig. 4: Graphs of reflectance versus wavelength for samples 16, 19 and 20

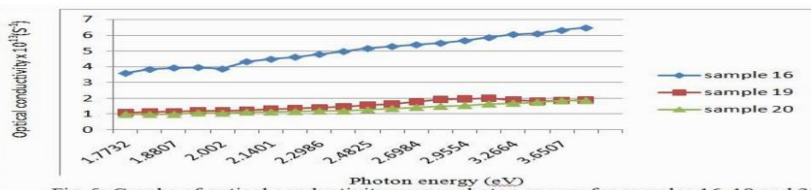


Fig. 5: Graphs of optical conductivity versus photon energy for samples 16, 19 and 20

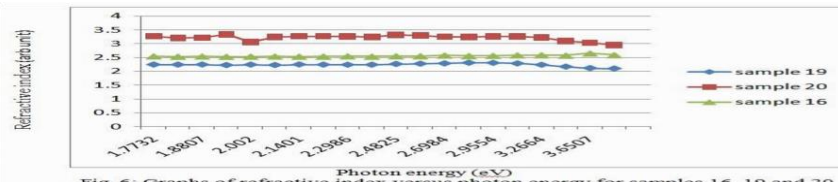


Fig. 6: Graphs of refractive index versus photon energy for samples 16, 19 and 20

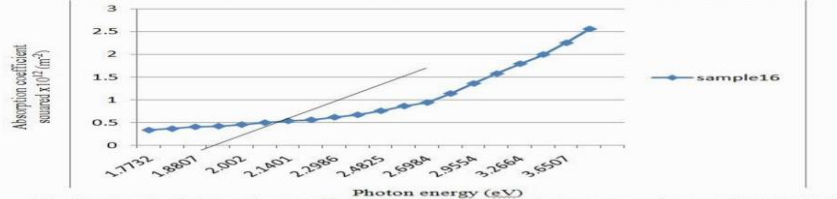


Fig. 7a: Graph of absorption coefficient squared versus photon energy for sample 16 (50°C)

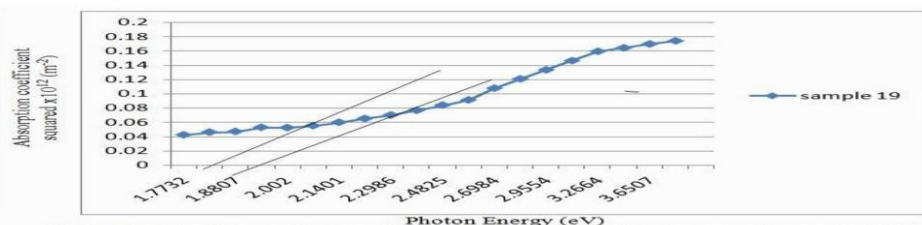


Fig. 7b: Graph of absorption coefficient squared versus photon energy for sample 19 (65°C)

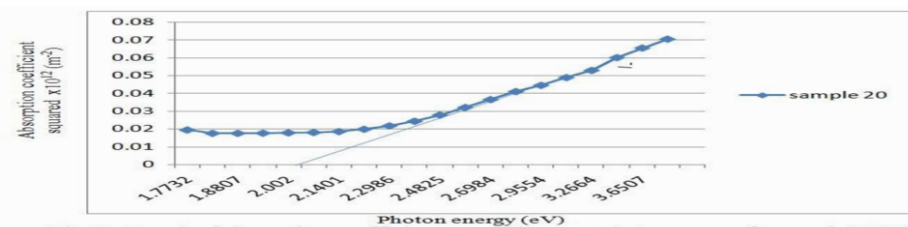


Fig. 7c: Graph of absorption coefficient squared versus photon energy for sample 20 (70°C)

CONCLUSION

The films of CuAlSe₂ were successfully deposited using chemical deposition technique onto commercial microscope glass substrates at variation of deposition temperature. The optical properties show that films could be useful in photovoltaic solar cell applications and thermal window coatings. The influence of deposition temperature in this research shows that: absorbance and optical conductivity increase as the deposition temperature decrease, but increase in reflectance and film thicknesses bring about increase in bath temperature. The energy band gap is in the range of 2.00 to 2.14 eV which shows that it is potentially useful for blue light-emitting diodes. The band gap energy decreases as the deposition temperature increases. It does agree with the fact that increase in temperature brings about decrease in difference between the conduction band minimum and valence band maximum which is called the energy band gap.

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