



EFFECT OF DIP TIME ON THE STRUCTURAL AND OPTICAL PROPERTIES OF CuAlSe_2 FILMS.

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ABSTRACT

Ternary semiconductor chalcopyrite films of CuAlSe_2 are prepared by chemical bath deposition technique on a microscopic glass substrates from an aqueous solution containing copper chloride, aluminium chloride and freshly refluxed sodium selenosulphate. The influence of dip time on the properties of CuAlSe_2 films was investigated. The X-ray diffraction analysis showed that the deposited films were polycrystalline with chalcopyrite structure having a strong orientation along the (200) plane. The surface morphology study revealed that the grains have cubic shape crystal. The band gap energy was decreased from 2.6 eV to 2.4eV as the dip time was increased from 12hours to 24hours. The film grown at 24 hours showed good crystallinity. It was also, uniformly distributed over the surface of the substrate with larger grain sizes. Therefore, the optimum deposition time for the synthesis of chemically deposited CuAlSe_2 films is 24 hours.

KEYWORDS: Chalcopyrite, CuAlSe_2 , chemical bath, x-ray diffraction, band gap energy.

I. INTRODUCTION:

The synthesis and study of properties of ternary semiconductor compounds has increased in recent years¹⁻⁴. Ternary semiconductor chalcopyrite are being studied intensively due to their application in optoelectronic devices and solar cells⁵. CuInSe_2 is the most known compounds of the family.

In the present case, the influence of dip-time on the chemically deposited copper aluminium selenide thin films has been investigated. The chemical bath deposition technique is a time saving, cost effective and economically reproducible technique that can be applied in large area deposition at low temperature. The use of complexing agent is very common in the preparation of thin films through chemical bath deposition. Researchers use various complexing agents such as thiourea⁶, ammonia⁸⁻⁹, triethanolamine¹⁰⁻¹¹, disodium ethylene diamine tetraacetate¹², ammonium hydroxide¹³, hydrazine¹⁴, sodium citrate¹⁵, and tartaric acid¹⁶⁻¹⁷ during deposition of thin films. Chemical bath deposition is based on the controlled release of metal ion (M^{2+}) is controlled by using a suitable complexing agent. The deposition begins with nucleation phase followed by growth phase in which the thickness of film increases with duration up to the terminal where film depletion into constituents ions occurs after a time¹⁸. Therefore, to achieve well-adhered films, optimization of the deposition condition is of paramount importance in chemical bath deposition.

The influence of dip time on the properties of CuAlSe_2 films was studied. The structural analyses of prepared films are performed by means of X-ray diffraction technique. Optical properties were examined by an UV-Visible spectrophotometer. An Olympus BH2-UMA microscope at 100 x magnifications was used to examine and produce photomicrographs of the samples.

II. MATERIALS AND METHODS:

Copper Aluminium Selenide thin films were deposited on glass slide by chemical bath technique using an aqueous solution prepared from 1M of CuCl_2 , 0.5M of AlCl_3 and freshly refluxed Na_2SeSO_4 . The pH of the solution was kept constant using 3.0ml of ammonium hydroxide while ethylene-diamine tetra-acetate was used as the complexing agent. The influence of dip time on the chemical bath deposited films was investigated under different deposition times from 12 hrs to 24 hrs.

At first, the CuCl_2 and Na_2SeSO_4 were mixed and complexed with EDTA, and then AlCl_3 solution was added. The dip time was varied while other variables remain constant.

Before the deposition, the glass slide was cleaned with dilute HCl and rinsed with distilled water. The cleaned slides were vertically suspended in the reaction baths with a holder for different dip time of 12hrs, 18hrs, and 24hrs, respectively.

The crystalline phases of the prepared films were examined by XRD analysis using an X-ray MD-10.3mini diffractometer with $\text{CuK}\alpha$ radiation wavelength of 1.5406. The microstructures of the film were observed using an Olympus BH2-UMA microscope at 100x magnification. The optical absorption spectra of prepared films were measured by a Janway 6405 UV-VIS model of the spectrophotometer.

III. RESULT AND DISCUSSIONS.

A. Structural Properties.

The X-ray diffraction patterns of CuAlSe_2 thin films deposited at varying dip times of 12hrs-24hrs are presented in figure 1. The onset of crystallization was observed in the film grown for 12hours with only one peak at 2θ value of 34.88° preferably oriented along (200) planes. The film grown for 18 hours showed two peaks at 2θ values of 34.88° along (200) and 59.6° along (311) plane. But the film deposited at 24 hours showed three peaks at 2θ values of 30.0° along (111), 34.88° and 59.6° along (200) and (311) planes respectively. The increase in intensity of XRD peaks with increasing dip time revealed the enhancement in crystallinity of the films. The observed lattice spacings d , are indexed with standard JCPDS data corresponding to the cubic phase (Card No: 01-078-4019). The pattern confirms the formation of chalcopyrite polycrystalline CuAlSe_2 films with preferential orientation along the (200) planes. The lattice constants of CuAlSe_2 is $a = b = c = 3.635\text{\AA}$. This is in good agreement with the standard data.

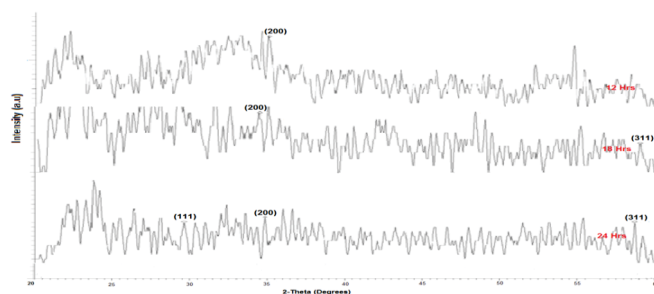


Fig 1 X-ray diffraction patterns of CuAlSe_2 thin films deposited at different dip times of 12 hrs, 18 hrs and 24 hrs.

B. Micrograph Analysis.

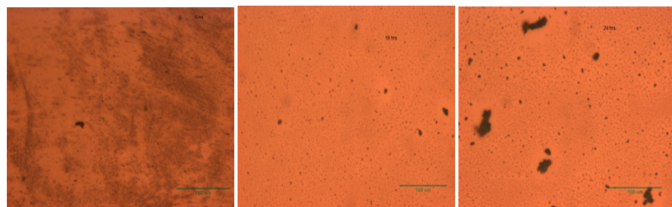


Fig. 2 Micrograph images for CuAlSe₂ thin films deposited for 12 hrs, 18 hrs and 24 hrs.

The surface morphology of the deposited CuAlSe₂ films at varying deposition times was studied and a systematic analysis was carried out at x100 magnification. Varieties of interesting morphologies were observed as shown in figure 2. The morphologies of the films at various deposition times reveal that the crystallites are of varying sizes and orientation. This property suggests that the particle grains are polycrystalline. Image-J for microscopy image analysis¹⁹ software was used to determine the average particle size of the films from the micrograph images of figure 2. The average particle sizes of 5.9 nm, 99.1 nm and 99.8 nm were obtained for CuAlSe₂ thin films. The film grown at 24 hours showed good crystallinity. It was also, uniformly distributed over the surface of the substrate with larger grain sizes

C. Optical Properties.

The optical properties of the films were determined from analysis of the measured absorbance spectrum. The absorbance spectra of CuAlSe₂ thin films which were deposited at room temperature at three different deposition times were recorded in the wavelength range of 340nm – 1100nm as shown in figure 3. The films deposited at longer time have high absorbance value while the films deposited at shorter time indicate low absorbance value. The spectra reveal low absorption in the lower photon energy (VIS-NIR regions). The high absorbance in the UV region makes CuAlSe₂ useful in forming p-n junction solar cells with other suitable thin film materials for photovoltaic applications²⁰ and a good window layer for solar cell application²¹. The low absorption of energy makes CuAlSe₂ films useful for optical components in higher laser window and multispectral applications, proving good characteristic image²².

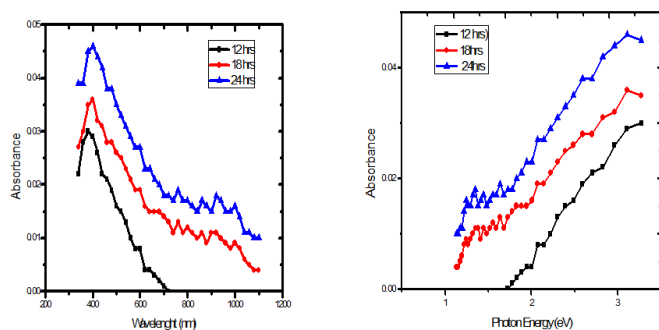


Fig. 3 Absorbance spectra of CuAlSe₂ thin films deposited at varying dip times

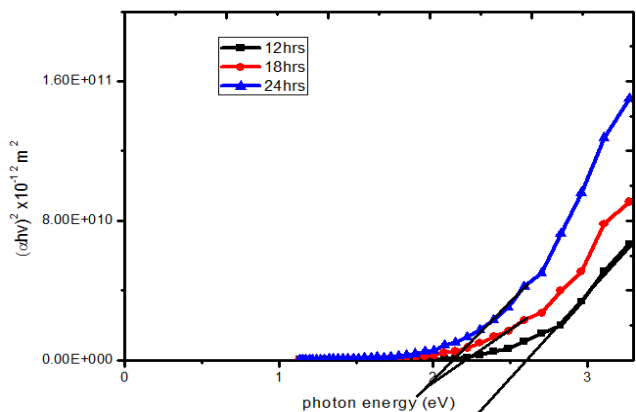


Fig. 4 Plot of (ahv)² versus hu of CuAl Se₂ film deposited at varying dip times.

Figure 4 shows the (ahv)² versus hu plots of CuAlSe₂ thin films deposited for dip times of 12hrs – 24hrs. The films increase gradually in a similar manner from near zero at 1.1eV to 0.6x10¹¹, 0.7 x10¹¹ and 1.4x10¹¹ at 2.4eV for thin films deposited at 12hrs, 18hrs and 24hrs respectively. Thereafter, they increase sharply at 2.5eV. The linearity of the plots indicates that the material is of direct band gap. The energy band gap values are 2.6eV, 2.5eV and 2.4eV for the films deposited for 12hrs, 18hrs and 24hrs respectively. This is in accordance with the findings of²³ whose range of band gap energy is between 2.4eV - 2.5 eV. The film deposited at longer time has low band energy while the film deposited at shorter time indicates high band energy value. The decrease in the band gap with increasing dip time can be viewed as increasing the energy of the electrons in the materials. Lower energy is therefore needed to break the bond. Reduction in the bond energy also reduces the band gap.

Table 1 Optical band gap values of CuAlSe₂ thin films deposited for different dip times.

Dip time (Hours)	Band gaps, Eg (eV)
12.00	2.60
18.00	2.50
24.00	2.40

IV. CONCLUSION:

CuAlSe₂ films have been obtained by chemical bath deposition technique. The CuAlSe₂ film deposited at longer time showed higher absorbance value. The energy gaps obtained showed that energy band gap decreased with increase in deposition time. XRD pattern of the deposited films showed clearly the cubic polycrystalline CuAlSe₂ films with chalcopyrite structure.

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