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The Optical and Structural Properties of Thermally Vaporized Composite Thin Films

In the current work, $CuAlSe_2$ alloys were fabricated by melting the stoichiometric weights of Cu, Al, and Se in a sealed quartz ampoule at a vacuum of about 3×10^{-2} mbar. The alloy is applied to a soda lime glass substrate, heated to various temperatures, and then thermally evaporated at a pressure of roughly 10^{-6} mbar. The thin layer has a thickness of 1200±100 Å. Thin films were polycrystalline with sphalerite structure but the bulk showed chalcopyrite structure throughout. An increase in the optical energy gap with substrate temperature and direct transitions in the thin layer were observed in the optical experiments. As the annealing period was raised to two hours, the films annealed at 200-400°C indicated an increase in the energy gap.

Keywords: $CuAlSe_2$; Thin films; Thermal evaporation; Optical energy gap
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1. Introduction

The preparation technique of thin films from solid materials is one of the most crucial methods for studying their physical characteristics. Since thin films are used in the fabrication of integrated circuits like capacitors, resistors, and diodes as well as high-reflective mirrors and electromagnetic detectors, they are important to both advanced applications and solid-state physics research. One of the most significant and well-preferred uses of thin films is the fabrication of solar cells due to their low production cost as they require less production requirements than other energy sources [1]. Due to their high energy band gap (2.67eV) and tri-crystalline form in the orthogonal chalcopyrite structure, which is comparable to the structure of sapphirite, the $CuAlSe_2$ compound family has recently gained the interest of many researches. These compounds can be used in solar cells with efficiencies up to 11% and as electromagnetic radiation detectors too [2,3]. The group I-III-VI compounds, such as $CuAlSe_2$, $CulnSe_2$, and others, have great technical significance because of their remarkable optical sunlight absorption. The basic absorption edge of an ideal semiconductor is the region where photons with energy at least equal to the optical energy gap are employed to activate the valence band [4]. In crystalline and polycrystalline semiconductors, there are direct transitions, where electrons move from the top of the valence band to the bottom of the conduction band without changing their wave vector. The absorption coefficient of these transitions (α_{dir}) is related to the optical energy band gap (E_{gopt}) by the following relatioship

$$\alpha_{dir} = B(hv - E_{gopt})^{\frac{1}{2}} \quad (1)$$

where B is a constant, and h is the energy of the incident photon

In crystalline and amorphous semiconductors, an indirect transition can occur when the electron wave vector is different before and after the transition. Transitions in semiconductors are unconstrained, however in crystalline semiconductors, the conservation of momentum principle imposes restrictions. The law of conservation of momentum is random because composition is unpredictable. The indirect absorption coefficient for each type of semiconductors is given if crystalline and polycrystalline semiconductors absorb photons to accomplish momentum conservation [3].

$$\alpha_{lnd} = \frac{c(hv - E_{gopt})}{e^{(E_{ph}/kT - s)}} \quad (2)$$

where E_{ph} is the energy of the absorbed photon, E_{gopt} is the optical energy gap, and c is a constant

2. Experimental Part

The pure stoichiometric weights of the constituents (Cu:Al:Se = 1:2:3) were combined in a sealed quartz tube to produce the alloy. The quartz tube was evacuated using a rotary pump to $3x10^{-2}$ mbar getting an evacuated tightly-closed tube as a capsule with the three contents. A convection oven was gradually and gently heated to 1100°C and the tube was left there for three hours. To guarantee a homogenous molten mixture and complete fusion of

the three elements, the oven is regularly stirred and set at 1100°C. After the capsule gradually cools to room temperature to extract the alloy ($CuAlSe_2$), some of its bulk is powdered and characterized by the x-ray diffraction (XRD) analysis to ensure the formation of the required alloy. A molybdenum (Mo) evaporation pot was continuously electrically charged and the evaporation chamber was evacuated to 10^{-6} mabr in order to perform the process at room temperature. This allowed for the growth of thin films by thermal evaporation using Balzer evaporation system. At a rate of 2 Å/s, the substance was evaporated. Consequently, the film preparation process was performed at room temperature. the film preparation process was carried out with variable deposition temperatures. The alloy was fabricated in the form of an ingot, which is then completely ground to produce usable alloy powder. A Phillips x-ray diffractomer was used in the scanning range (2θ) of 20°-70°, and the thin films prepared from the same alloy were examined using the same XRD apparatus. The film thickness was measured using a quartz crystal monitor and the optical interference method [5].

3. Results and Discussion

By comparing the Bragg's reflections of the deposited films and alloy powder with the American Standard for Testing Material (ASTM) cards, the composition of the alloy (bulk) was verified by analyzing the XRD patterns. It was found that these patterns belong to the compound $CuAlSe_2$. These patterns are displayed in Fig. (1) for substrate temperatures (T_s) of 150°C, 250°C, and 350°C.

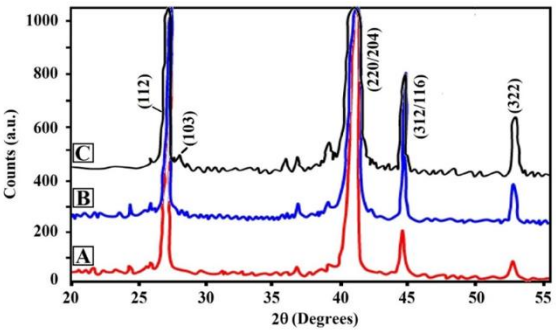

Fig. (1) XRD patterns of the samples deposited at different substrate temperatures (a) 150°C, (b) 250°C, and (c) 350°C

By increasing the substrate temperature, the composition of the prepared samples was sphalerite cubic with a lattice dimensions of a=5.0364Å and c=10.5440Å [6,7]. The substrate's composition is sphalerite cubic with a lattice dimension of a=5.0364Å, and by raising the temperature, the sample becomes much more porous (c=10.5440Å). The XRD patterns of the thin films annealed at 200°C or 400°C for two hours with thickness of 1200±1100Å are displayed in figures (2) and (3). These figures showed an increase in the intensity of some peaks and a decrease in the intensity of others when compared with Fig. (1) for unannealed films. The reason for this result is attributed to the growth of crystalline grains due to the coalescence of the grains with each other during the annealing process, which will lead to an increase in the diffraction intensity of some peaks, whereas the decrease in the intensity of some other peaks is due to the fact that this coalescence process will lead to the formation of separate islands (discrete islands), the distances between which are rather wide, especially when the thickness of the deposited film is small, and this is consistent with reference [9].

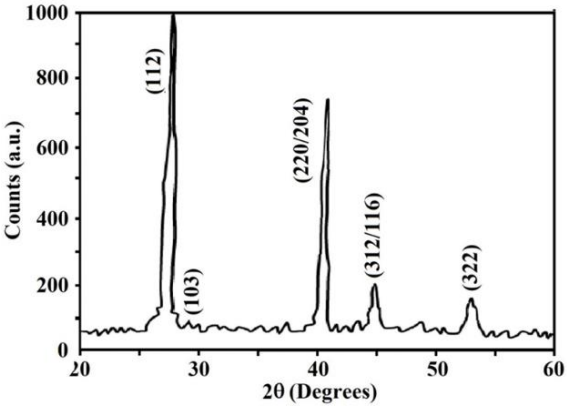

Fig. (2) XRD pattern of $CuAlS_2$ thin film annealed at 200°

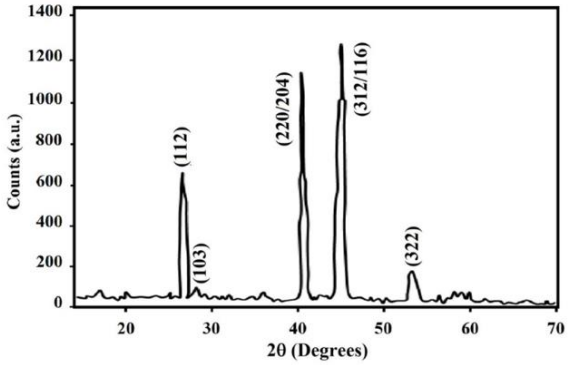

Fig. (3) XRD pattern of $CuAlS_2$ thin film annealed at 400°

The relationship between $(\alpha h\nu)^2$ and incident photon energy ($h\nu$) is depicted in Fig. (4). It is observed that the films prepared at high temperatures exhibit increased crystallization, as the composition of the $CuAlSe_2$ films is greatly influenced by the substrate temperature during film deposition. The activation energy of the deposited particles increases with the intensity and height of the Bragg's peaks. This energy is required for the deposited particles to reach sites on the substrate with the least energy loss in order to be more stable. As a result, during the evaporation process, the films prepared at temperatures 150-350°C exhibit phase transition from orthogonal chalcopyrite to cubic sphalerite. These findings agree with those of references [7,8], who found that deposition of thin films at lower temperatures results in the growth of films composed primarily of sphalerite. We observe

that the $CuAlSe_2$ films are of direct transition, which is consistent with the results of references [4,10]. Also, the values of optical energy gap were in agreement with those of reference [4], who prepared $CuAlSe_2$ films at temperatures between 300 and 400°C using a spray deposition method. The rise in the number of crystalline grains and the increase in film crystallization were the reasons given for the increase in the optical energy gap with increasing deposition temperature. The absorption edge is obviously impacted by the annealing process. The effect of film annealing at 400°C for two hours is depicted in Fig. (5). The optical energy gap has changed to 2.65eV for films annealed at 200°C and 400°C, as shown in this figure. The annealing process removes structural flaws and increases the grain size, which explains the increase in absorbance due to the increase in granular boundaries. This is consistent with references [11-14].

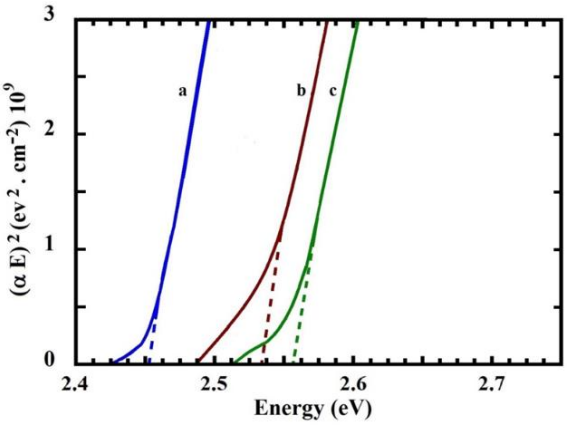

Fig. (4) Relationship of $(\alpha h\nu)^2$ with incident photon energy ($h\nu$) for thin films prepared at different substrate temperatures (a) 150°C, (b) 250°C, and (c) 350°C

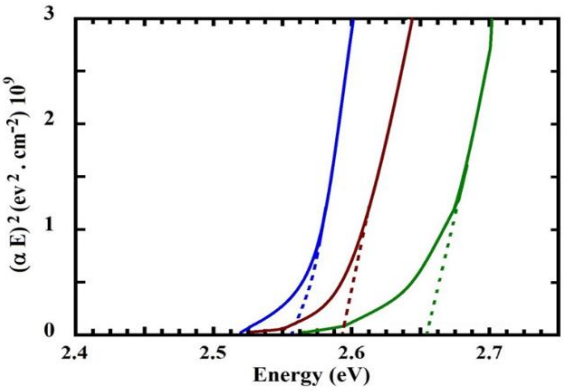

Fig. (5) Effect of annealing temperature on the energy band gap of the thin films: (a) not annealed, (b) annealed at 200°C, and (c) annealed at 400°C for two hours

4. Conclusion

The thin films deposited at high temperatures were found much more crystalline. During the evaporation process, the orthogonal chalcopyrite composition of the films formed at temperatures between 150 and 350°C has converted into cubic sphalerite, causing a phase transition. The growth of crystalline grains is a result of the grains coalescence during the annealing process. The absorption edge is clearly impacted by the annealing process, which decreases structural flaws and enlarges the grains.

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