Deposition, Structural, Electrical and Hall Measurement Properties of Chemical Bath Deposited $CuInSe_{2-x}S_x$ (x=0.5) Thin Films

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Abstract: A thin film of the Quaternary alloy semiconductor compound $CuInSe_{2-x}S_x$ was made using the chemical bath deposition method. The solution used included $CuCl_2$, $InCl_2$, thiourea (H_2N-CS-NH_2), and Na_2SeSO_3. The structure of the thin film was studied using X-ray diffraction. The results showed that the film has a chalcopyrite structure and is made of many small crystals. The orientation of these crystals showed a preference for the (112) direction. The electrical resistivity of the thin film material was measured by using two probe method in the temperatures range 303 K and 473 K. The Arrhenius equation was used to find the activation energy. The I-V curves for the $CuInSe_{2-x}S_x$ thin films were drawn both in the dark and under different light intensities. These curves showed diode-like behavior, indicating that an Ag contact forms a Schottky diode with the $CuInSe_{2-x}S_x$ film. The Hall effect was used to find the mobility and carrier concentration of the film at room temperature, and the Van der Pauw-Hall method was used for these calculations.

Keywords: *Chemical Bath Deposition, $CuInSe_{2-x}S_x$ Thin Films, Electrical Properties, Hall Measurement.*

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I. INTRODUCTION

$CuInSe_{2-x}S_x$ is a group of four-element semiconductor materials called chalcogenides. These materials have a crystal structure similar to chalcopyrite ($CuFeS_2$). Chalcopyrite materials are among the most promising for uses like making solar cells. Copper indium diselenide ($CuInSe_2$) is prototype member of the family of I-III-VI_2 chalcopyrite semiconductors. Chalcopyrite semiconductors like CuInSeTe, CuInSeS, and CuInSeTe have attracted a lot of interest because they are suitable for use in solar cells. The compound $CuInSe_{1-x}Te_x$, where x is between 0 and 1, is also a member of this group.There are several methods used to make CuInSeS thin films. These include the arrested precipitation method, chemical vapour deposition, DC or RF magnetron sputtering, electro deposition, vacuum evaporation, flash evaporation, and spray pyrolysis. Compared to other methods, the chemical bath deposition method (CBD) is the very simplest and easy. It allows for making large area films at a low cost and causes very little material waste. It also doesn't require handling harmful gases. This process uses very little energy, making it cost-effective. CBD has been used in many applications for making various binary and ternary semiconductors. However, its use for making ternary and quaternary compound semiconductors hasn't been fully explored. This is because it is difficult to control the composition and process in a way that gives high-quality, reproducible films. This article focuses on the chemical deposition method and the characterization of polycrystalline thin films of $CuInSe_{2-x}S_x$ with a specific composition (x = 0.5) near the ideal stoichiometric ratio. The study reports on the structural, electrical properties, and I-V characteristics in both dark and light conditions, along with Hall measurements of this material.

II. EXPERIMENTALS

➢ *Substrate Cleaning:*

Glass slides of size 7.3 cm x 2.5 cm x 0.1 cm (blue star make) were used as a base for growing $CuInSe_{2-x}S_x$ (x=0.5) thin films. To get good thin films with chemical bath deposition (CBD), the slide surface must be very clean. If the surface has dirt or other materials, it can create places where the film isn't growing properly. These areas might have holes or cause the film to not stick to the slide. Poor adhesion between the film and the slide happens when there's a barrier, like oil, grease, or unwanted layers, on the surface. These materials need to be removed. The following steps were taken to clean the slides:

- The slides were first washed with water.

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- They were then placed in a chromic acid bath and ultrasonicated for 1 hour to remove metal impurities and dust.
- Next, they were washed with hot deionized water to get rid of the chromic acid.
- The slides were again ultrasonicated in an acetone bath for 5 minutes to remove oil and grease.
- They were then washed with deionized water.
- This process was done at least 1 to 2 times.Finally, the slides were rinsed with deionized water, dried in an oven, and kept in a dust-free airtight container.

➢ *Preparation of Solution:*

All the chemicals and reagents used were of A.R. grade. The chemicals included copper chloride [$CuCl_2$], indium trichloride [$InCl_3$], sodium sulphide [Na_2SO_3], ammonium hydroxide [NH_4OH], triethanolamine [$C_6H_{15}NO_3$], thiourea [NH_2-CS-NH_2], elemental selenium [Se], and ammonia [NH_3]. For the thin film deposition, 0.1M solutions of $CuCl_2$, $InCl_3$, NH_2-CS-NH_2, and Na_2SeSO_3 were made using double distilled water as the solvent. Triethanolamine was added to help with complexing, and ammonia was used to increase the pH to 11.3.

➢ *Deposition of* $CuInSe_{2-x}S_x$ *(x=0.5) Thin Films:*

$CuInSe_{2-x}S_x$ (x=0.5) thin films of different compositions were deposited using chemical bath deposition. The effects of deposition time, temperature, and concentration of the source materials were studied.Copper chloride, indium trichloride, NH_2-CS-NH_2, and sodium sulphide were used to provide the Cu^{2+}, In^{3+}, S^{2-}, and Se^{2-} ions. Elemental selenium powder was dissolved in a sodium sulphide solution by heating and adding powder selenium slowly in to solution of sodium sulphide i.e. by reflux method. Copper chloride and NH_2-CS-NH_2were prepared in double distilled water or the Indium trichloride was mixed with citric acid. Triethanolamine was added as a complexing agent to the copper and indium solutions. The solutions of $CuCl_2$, $InCl_3$, Na_2SeSO_3, and NH_2-CS-NH_2were mixed in a 100ml beaker. The pH was adjusted to 10.3 using ammonia. The solution was stirred to make it uniform. The cleaned slides were placed in a holder and positioned vertically in the beaker, which rotated at 50 rpm for 80 minutes at a bath temperature of 50°C.After the process, the slides were removed from the bath, washed with distilled water, dried in the air, and stored in an airtight container. Thin films with different compositions were made using optimized process parameters for x=0.5. The color of the films was seen as brown to gray. The films stuck well to the slides. The thickness was measured using a Michelson interferometer, and it was around 0.1743 µm. The electrical resistivity was measured using the two-probe method. Hall setup is used to determine Hall voltage with alternating current and magnetic field directions. XRD patterns were put down by using an AXS Germany D8 Advanced X-ray diffractometer with CuK_α radiation (λ = 1.5423 Å). The diffractometer was operated at 40 kV and 100 mA.

➢ *X-ray Diffraction (XRD) Studies:*

Fig. 1 shows the XRD patterns of $CuInSe_{2-x}S_x$ (x=0.5) thin films that were heated at 300°C in air for 30 minutes. The XRD patterns show that the thin films are polycrystalline and have a preferred (112) orientation. Similar results have been found for chalcopyrite $CuInSe_2$ thin films by other researchers. The diffraction peaks from (112), (200), (201), (220), (312), and (116) show the chalcopyrite structure of the material. The (201) peak indicates the presence of a binary phase like Cu_2Se. The (312) and (116) peaks are related to In_2S_3 and In_2Se_3 phases. The data was compared to standard data (JCPDS 36-1731). The full width at half maximum (FWHM) became smaller value because of FWHM narrower as the concentration of Se increased. For x=0.5, the FWHM for the (112) peak was 0.3920. Previous studies showed that as the composition x increases, the grain size of $CuInSe_{2-x}S_x$ films increases. The lattice parameters a and c depend on composition. For x=0.5, a = 5.301 Å and c = 11.427 Å.

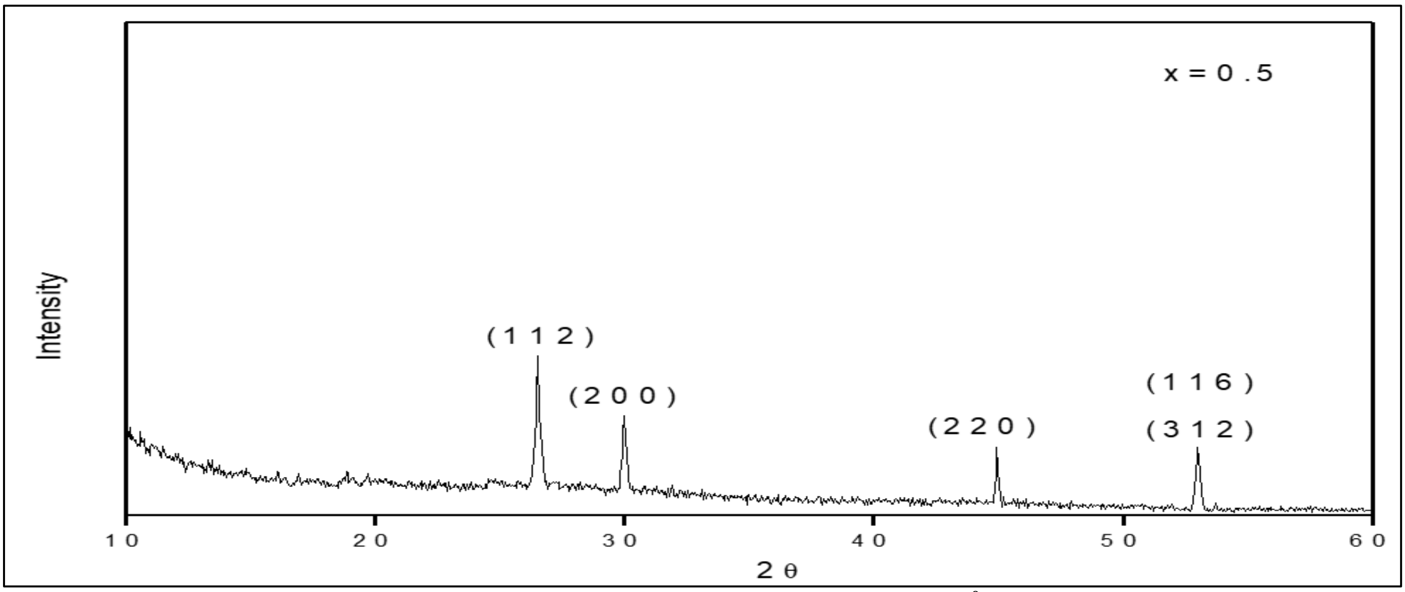

Fig 1 XRD Patterns of $CuInSe_{2-x}S_x$ (x=0.5) Thin Films Annealed at 300^0C in Air for 30 Min

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III. ELECTRICAL PROPERTIES

➢ *Electrical Resistivity:*

The electrical resistivity of $CuInSe_{2-x}S_x$ (x=0.5) thin films was measured using the two-probe method. Fig. 2 shows a plot of log (ρ) versus the reciprocal of the film temperature (1000/T) for annealed $CuInSe_{2-x}S_x$ (x=0.5) thin films. The resistivity decreases linearly with increasing temperature, indicating that the films have semiconductor behavior. The activation energy of the material was calculated using a known formula [20].

$$\rho = \rho_0 \exp\left(\frac{-E_a}{kT}\right)$$

The activation energy for the composition value (x=0.5) is 0.193 eV. Resistivity varies from 8.7 x 10^2 Ω-cm to 2.5 x 10^4 Ω cm ; this low value of resistivity is due to the formation of Cu_2Se and Cu_2S phases in the film material, which is observed in XRD analysis of $CuInSe_{2-x}S_x$ (x=0.5) thin film samples. But the resistivity of $CuInSe_{2-x}S_x$ (x=0.5) thin films is still higher as compared with reported values in literature [21,22,23], because the thin films of $CuInSe_{2-x}S_x$ (x=0.5) is deposited by chemical bath deposition method, which gives higher values as compared the films deposited by other methods i.e. electrodeposition, selenization, or by vacuum deposition methods. The resistivity of the $CuInSe_{2-x}S_x$ (x=0.5) thin films decreases with increase in temperature; it shows the semiconducting behavior of the $CuInSe_{2-x}S_x$ (x=0.5) thin films.

➢ *I-V Characteristics of $CuInSe_{2-x}S_x$ (X=0.5) Thin Films:*

$CuInSe_{2-x}S_x$ (x=0.5) thin film annealed at 300^0C were studied for I-V characteristic properties in dark and by illuminating the sample with light of intensity 60 mW/cm^2, 100 mW/cm^2 and 140 mW/cm^2 as shown in fig 3. It is clear that I-V characteristics are of diode nature, indicating that silver contact forms the Schottky diode between Ag/$CuInSe_{2-x}S_x$. It is interesting to observe that the I-V characteristics in the dark exhibit a rectifying nature, i.e., current in the one direction (Ag +ve, Ist quadrant) is higher than in the opposite direction (Ag –ve, IIIrd quadrant). From the I-V plot, it is very much clear that the films gives good response to the light and hence indicating that the $CuInSe_{2-x}S_x$ films can be employed in photodetector application. For the photodetector application of the film, photosensitivity is an important parameter, which calibrates directly the quality of the photodetector. The photosensitivity (S) is calculated by using the equation as[24],

Where R_d and R_L are the resistances in dark and under light, respectively.

Fig. 4. Shows the plot of photosensitivity against the illuminated intensity. Thus, it can be concluded that the enhancement of the photoconductive sensitivity is due to the increase in electron hole (E-H) pairs with the intensity of the incident light.

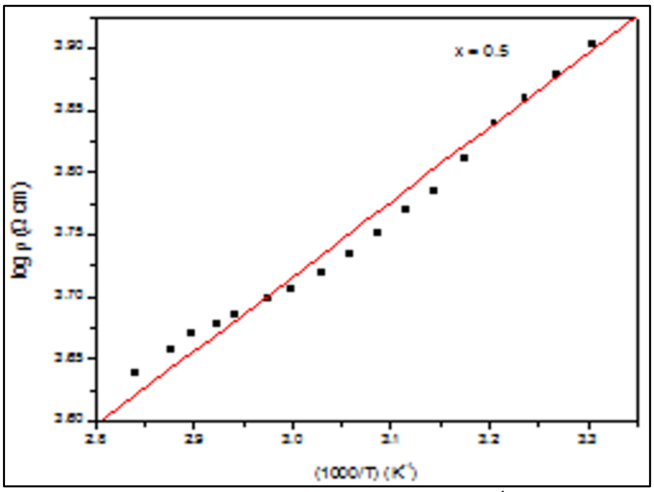

Fig 2 Plot of Log ρ (Ω cm) Versus 1000/T (K^{-1}) of $CuInSe_{2-x}S_x$ (x=0.5) Thin Films Annealed at 300^0C in Air for 30 Min.

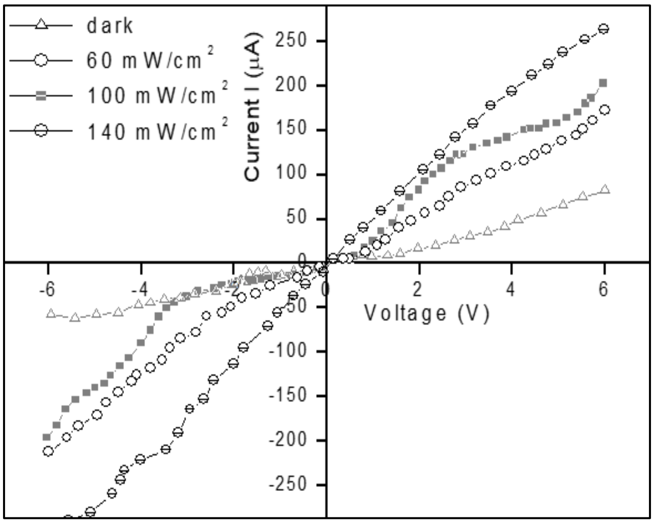

Fig 3 I-V Characteristics of $CuInSe_{2-x}S_x$ (x = 0.5) Thin Films in Dark and Different Light Intensity.

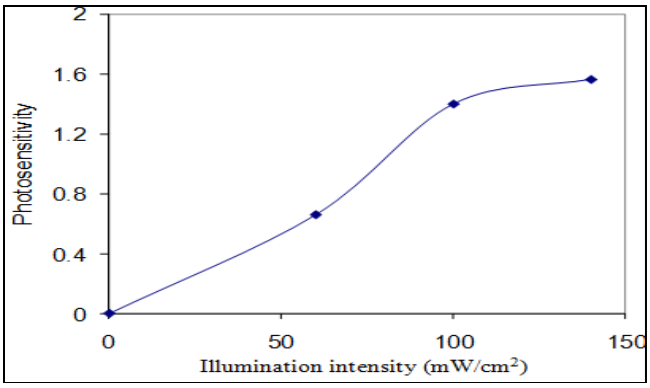

Fig 4 Photosensitivity Verses Illumination Intensity for $CuInSe_{2-x}S_x$

(x = 0.5) thin film

➢ *Hall Mobility and Carrier Concentration at Room Temperature:*

$CuInSe_{2-x}S_x$ (x=0.5) thin films that were heated to 300°C were studied using Hall effect measurements. The Hall coefficient was measured using the Van der Pauw-Hall

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technique at room temperature (25°C). The Hall mobility and the number of charge carriers were calculated. The Hall mobility at room temperature was found to be 1.92 cm² V^{-1} s^{-1}, which is similar to the values calculated by Soliman (26) for thin films made by vacuum evaporation. The Hall measurement also confirmed that the material has P-type conductivity (27).

IV. CONCLUSION

We conclude that $CuInSe_{2-x}S_x$ (x=0.5) polycrystalline thin films can be made using a simple chemical deposition method. The structure of the thin films was studied using Xray diffraction. The structure is of the chalcopyrite type with a unit cell size of a = 5.626 Å and c = 11.353 Å. The films grew mainly in the 112 direction. The grain boundary effect was also observed at low temperatures. The resistivity of the CuInSe2-xSx (x=0.5) thin films decreases as the temperature increases, showing that the films behave like semiconductors. The resistivity ranges from 8.7×10^2 Ω·cm to 2.5×10^4 Ω·cm. The activation energy for the composition with x=0.5 is 0.193 eV. The Hall mobility at room temperature was found to be 1.92 cm² V^{-1} s^{-1}.

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