

Structural and Electrical Properties of Copper Sulfide (CuS) Thin Films doped with Mercury and Nickel impurities.

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Abstract: Chemical bath deposited copper sulfide (CuS) thin films were doped with varying concentrations of mercury (Hg) and nickel (Ni) impurities (0.01-0.03M) on glass substrates at room temperature of 27 °C. X-ray diffraction (XRD) and four-point probe techniques were used to analyze the structural and electrical properties as well as the thickness of the doped CuS thin films. The XRD results reveal that the films have mono-crystallite structure with broadening of the diffraction peak by both impurities. Values of the Bragg's angle obtained were $2\theta = 29.28^\circ$ for the diffraction peak of Ni impurities and $2\theta = 27.86^\circ$ for the diffraction peak of Hg impurities as compared to un-doped CuS thin films whose diffraction peak occurred at $2\theta = 23.71^\circ$. The electrical resistivity of the films dropped from about 2000 Ω -cm for the un-doped CuS thin film to zero value for 0.01M of Ni impurities and then reversed from negative value back to zero for Ni impurities of equal to or greater than 0.02M concentration. For Hg impurities, the electrical resistivity first rose to 6,600 Ω -cm for 0.01M impurity, then dropped symmetrically back to 2000 Ω -cm for 0.02M impurity and gradually decreased with higher concentrations of Hg impurities. Corresponding variations in electrical conductivity, dielectric constants and film thickness with impurity concentrations are also reported in this paper.

Keywords: XRD, four-point probe, Hg and Ni impurities, diffraction peak, Bragg's angle.

I. Introduction

Copper sulfide is a p-type semiconducting material which belongs to I-VI compound semiconductor metals. Chalcogenide thin films of copper sulfide have received particular attention since the discovery of the CdS/CuS heterojunction solar cell in 1954 [1]. Other applications of CuS thin films include laminated glazing, photo-thermal conversion, electro-conductive electrode, microwave shielding and solar control coatings [2-6]. It is also used in photo-detectors and photovoltaic applications.

Electrical resistivity and conductivity of CuS thin films are dependent on various film and growth parameters including film composition, film thickness and impurity concentrations among others [7-11]. In this paper, the effects of molar concentrations of Hg and Ni on the electrical resistivity, conductivity and dielectric constants of CuS thin films prepared by CBD technique have been investigated. Also presented are the effects of the impurity concentrations on the film structure and thickness.

II. Experimental Details

Analytical grade reagents used for the CuS thin film deposition include copper sulphate (CuSO₄) as the precursor for copper ions, tri ethanol amine (TEA) as a complexing agent, thiourea (CS(NH₂)₂) as the precursor for sulfur ions and ammonia as the pH adjuster. Glass substrates were degreased with hydrochloric acid (HCl) for 48 hours, washed in cold water with detergent, rinsed with distilled water and dried in air for some minutes.

Then 7.5 ml of 0.755M of already prepared tri ethanol amine was measured out with clinical syringe and poured into 100 ml beaker that already contained 15 ml of 0.1M CuSO₄ solution. The mixture was stirred, after which 30 ml of thiourea solution was measured and added to the beaker with constant stirring. Finally, 4.5 ml of ammonia (NH₃) was added to the mixture.

Cleansed glass substrates were then inserted vertically into the reaction bath with the help of a synthetic foam/holder, which also partly covered the top of the beaker containing the bath. The bath was left undisturbed for 3 to 5 hours at a constant room temperature of 27 °C. This was followed with varying concentrations of mercury chloride and nickel chloride, the sources of nickel and mercury impurity ions, which were mixed separately with copper sulphate in different beakers and stirred thoroughly. Other reagents were orderly added as in the case of copper sulfide deposition. The mixtures were again thoroughly stirred and cleansed glass substrates were inserted and left undisturbed for hours for the deposition of the doped thin films. After deposition, the substrates were taken out, rinsed in distilled water, dried in air and stored for analyses.

III. Results and Discussion

The analyses of the CuS thin films were performed using X'PERT PRO diffractometer with CuK _{α} radiation of wavelength 1.54068Å in the 2 θ scanning mode to record the XRD data and Vander Pauw Four-

Point probe machine for the film thickness and resistivity measurements. Fig. 1 (a and b) show the increase in film thickness with impurity concentrations for both Hg and Ni impurities.

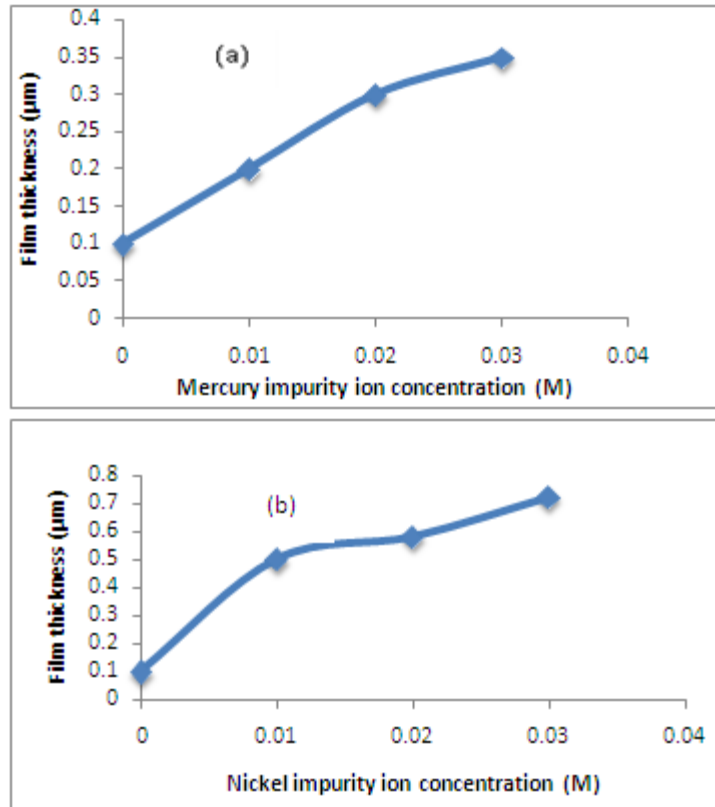


Fig.1: Variation in film thickness of CuS thin films with (a) Mercury impurities (b) Nickel impurities

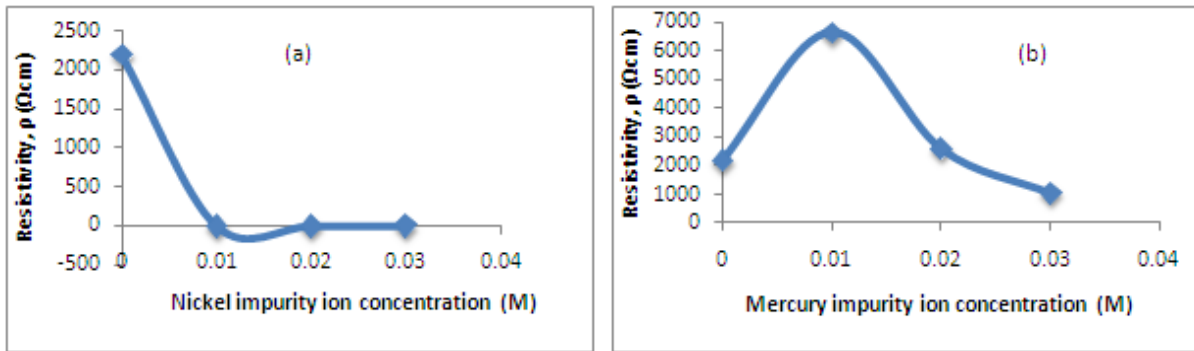


Fig.2: Variation in resistivity of CuS thin films with (a) Nickel impurities (b) Mercury impurities.

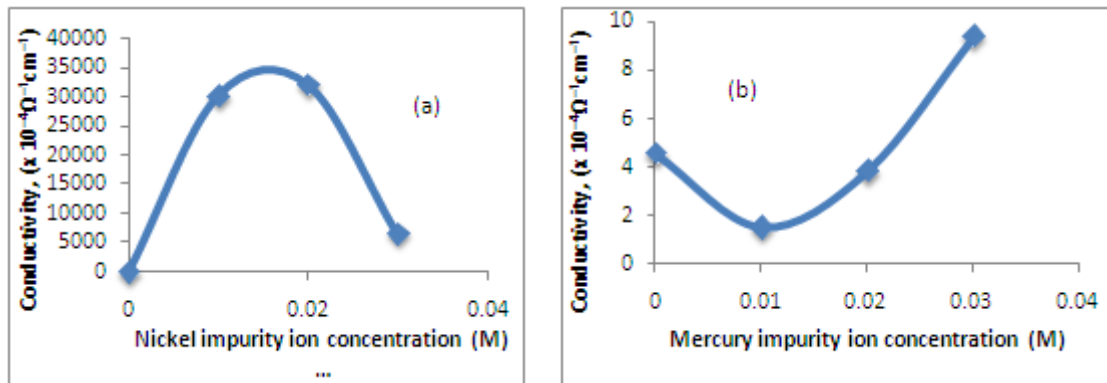


Fig. 3: Variation in conductivity of CuS thin films for (a) Nickel impurities (b) Mercury impurities.

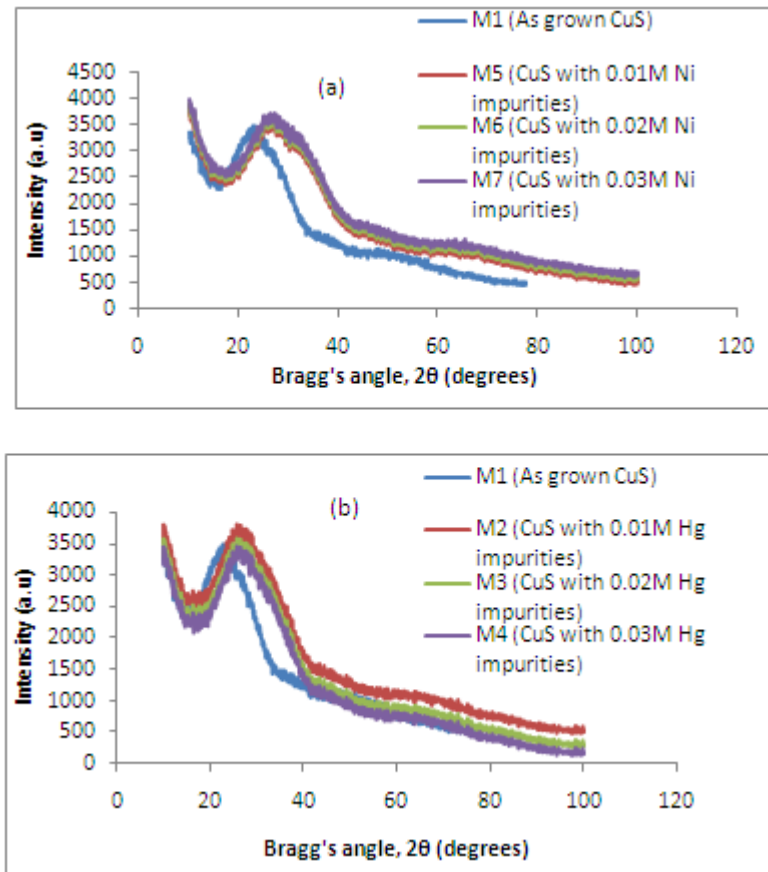


Fig. 4: XRD patterns for CuS thin films for (a) Nickel impurities (b) Mercury impurities.

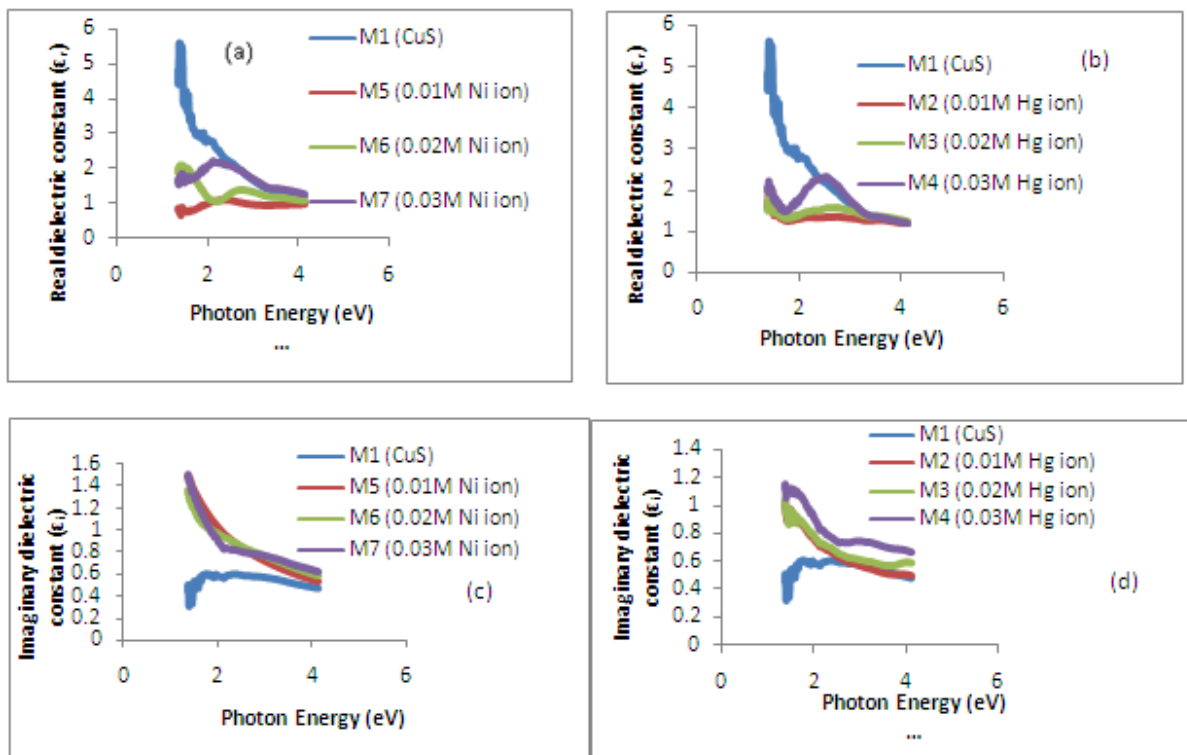


Fig. 5: Real and Imaginary dielectric constants for CuS thin films with (a and c) Nickel impurities (b and d) Mercury impurities.

Figures 2 and 3 respectively, show the variations in the resistivity and conductivity of the doped CuS thin films. In Fig. 2(a), 0.01M of Ni impurities decreased the resistivity from un-doped value of 2000 Ω -cm to zero and maintained zero value for Ni concentrations equal to or greater than 0.02M, while in Fig. 2(b), 0.01M of Hg impurity first increased the resistivity of the film from 2000 Ω -cm to about 6.600 Ω -cm, then dropped symmetrically back to 2000 Ω -cm for 0.02M Hg concentration and decreased further for higher concentrations. The corresponding conductivity values are as shown In Fig.3.

Figures 4 (a and b) show the XRD patterns for Ni and Hg impurities indicating peak broadening for both impurity concentrations. The figures also show that the peak broadening increases slightly with increase in Ni impurity concentration at $2\theta = 29.28^\circ$ and decreases with increase in Hg impurity concentrations at $2\theta = 27.86^\circ$ while the diffraction peak for the un-doped CuS thin film remains at $2\theta = 23.71^\circ$. The peak broadening is indicative of formation of smaller crystallite sizes.

Finally, Fig. 5(a-d) show the effects of Ni and Hg impurities on the real and imaginary dielectric constants of the thin films of copper sulfide.

IV. Conclusion

The deposition and analyses of structural and electrical properties of copper sulfide (CuS) thin films doped with varying concentrations of mercury and nickel impurity ions have been carried out successfully. XRD results reveal mono-crystallite structures for both impurities with diffraction peak broadening. The film thickness also increased with impurity concentration for both impurities. The resistivity of the CuS thin films decreased to zero for 0.01M Ni impurity from 2000 Ω -cm for the un-doped thin film, while Hg impurities produced first an increase to 6,600 Ω -cm, then a decrease in the resistivity of the thin films with increase in impurity concentration. The effects of the impurities on the electrical conductivity and dielectric constants of the thin films are as reported in this paper.

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