Investigation on Optical Properties of CuS and Zn Doped CuS Thin Films by Chemical Bath Deposition Method

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Abstract: *For decades copper sulfide has been considered as the most superior optical and semiconductor material. An attempt has been made to prepare bare and Zn doped CuS thinfilms by simple chemical bath deposition method. The prepared samples were characterized by XRD, UV and PL to identify and study its structural and optical properties. Results of XRD analysis confirmed the formation of CuS of Covellite phase. Optical properties were studied and the material exhibits a band gap of 2.41 eV and 2.39 eV for pure and Zn doped samples respectively.*
Keywords: *Copper Sulphide, Co-vellite, band gap.*

I. Introduction

Cu_xS is an II-IV group compound which is one of the most interesting materials, for it has semiconducting properties exist in several crystallographic and stoichiometric forms. Owing to its electrical conductivity and optical bandgap, it is mainly used in solar cell applications[1]. Based on the various parameters, Copper Sulfide exhibits different crystallographic orientation. Copper Sulfide is found to be existing in two forms: "Copper rich phase" and "Copper poor phase". They are chalcocite (Cu_2S), djurlite ($Cu_{1.96}S$), digenite ($Cu_{1.8}S$), anilite ($Cu_{1.75}S$) and co-vellite (CuS). Out of all these stoichiometric forms, co-vellite comes under copper poor phase [2].

There are several techniques used to prepare copper sulfide thinfilms [3]. They are spray pyrolysis, solid state reaction, vacuum evaporation, reactive magnetron sputtering, atomic layer deposition (ALD), activated reactive evaporation, chemical vapour deposition (CVD), chemical bath deposition (CBD) etc. Among these methods, chemical bath deposition is selected for the present work, for the method is simple, economic, non-pulling, and capable to attain large area coating [16]. CBD method is convenient for preparing homogenous and smoother thin films with required thickness with different dopents. In general, copper sulfide pentahydrate and sodium thiosulfate are selected as raw material to prepare copper sulfide thin films. Zinc chloride is used as dopent and EDTA is used as a clamping agent. Even though Zinc is used as the dopent, there is no report available in this regard. Thus, this study aims at making a report on chemical bath deposited copper sulfide thin films with zinc doped films, based on the investigation done using different techniques.

II. Experimental

2.1. Preparation of Copper sulfide (CuS) thin films:

Analytical-grade compounds are used to prepare the samples. Copper sulfide pentahydrate and sodium thiosulfate are taken as raw materials to prepare copper sulfide thin films. As a typical procedure 1:1 ratio of the raw materials are dissolved in 25ml of deionised water, and then 25 ml EDTA solution is added to the mixture as a clamping agent. Then, Ammonium hydroxide was added to maintain the pH of solution at 3. Finally the resulting solution was stirred for several minutes to maintain the pH value. After stirring for several minutes, pretreated substrates were immersed into the prepared bath at 50^0C temperature. While copper sulfide thin films are still prepared, the zinc is added as the dopent material. When the final material is obtained the substrates are removed and rinsed with deionized water and dried in air at room temperature for further characterization.

2.2. Characterization

The samples were characterized using X-Ray diffractometry (XRD) and optical analysis (UV-Vis spectrometry). XRD was performed using XPERT-PRO model.

III. Result And Discussion

3.1. Structural Analysis

The XRD of the deposited CuS thin film and zinc doped copper sulfide thin films were grown on glass substrates at pH 3. The broad hump in the films, 2θ ranges 15-35° due to the glass substrates. The XRD patterns clearly indicates that as deposited CuS thin films and zinc doped CuS thin film reveals crystalline nature with the preferred orientation along (1 2 4) and it is exactly matches with JCPDS card no 41-0959.

The deposited and zinc doped thin films contains single phase tetragonal primitive co-vellite phase of CuS. The best crystallinity is obtained for the zinc doped CuS thin films deposited at pH=3. Their crystalline structure exhibits corresponding to (1 2 4), (0 1 9) and (1 2 4), (2 0 0) planes. There is a change in lattice parameter CuS value when Zinc is doped with CuS. This is because of the ionic radius of Zn^{2+} [0.74] is larger than that of Cu^{2+} [0.73]. From the XRD data there is an increase in grain size for Zn doped CuS thin films. This is mainly due to the incorporation of Zn atoms in the films.
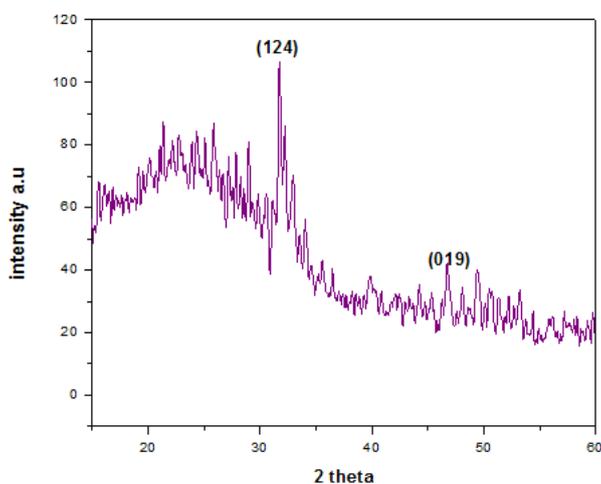

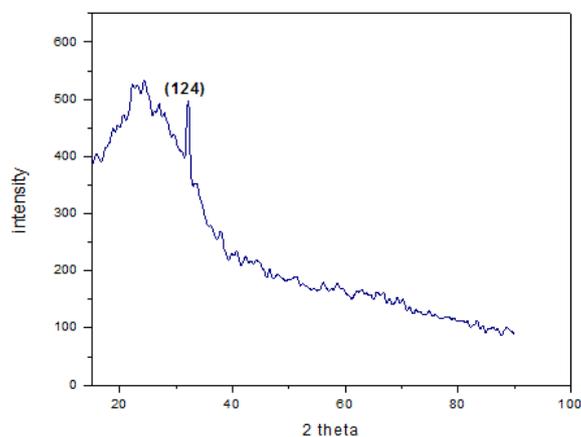
Fig.1 XRD spectrum of CuS thin film

Fig. 2 XRD Spectrum of zinc doped CuS thin films

The XRD shows that intensity of peak increases with the incorporation of Zn atoms to the material. The lattice parameters are calculated for the deposited and zinc doped CuS thin film samples are found to be in excellent agreement with the standard value and the lattice parameter are calculated for the zinc doped CuS thin film samples are found to be in excellent agreement with increase the value. The grain size is increased in zinc doped copper sulfide thin film. The micro structural parameters such as grain size, micro strain, and dislocation density are calculated from XRD data. From the deposited result, it is clear that changing parameters of dislocation and strain are directly proportional to each other, as in the zinc doped CuS.

Table 1: Structural parameters of chemically deposited CuS and Zinc doped CuS thin films

Sample	Grain size(nm)	Lattice parameter (Å)		Cell volume (Å)^3	Dislocation density (10^{15}Lines/m^2)	Strain (10^{-3}M)
		a	c			
CuS	286.2622	7.893	18.19	1132.36	1.2203	1.2425
CuS+ Zn	360.3442	7.290	21.41	1138.16	7.7013	0.9839

3.2. Optical Analysis
3.2.1. UV-Spectroscopy

The optical properties of CuS and zinc doped CuS thin films deposited on glass substrates are determined from the absorbance (A) and transmittance (T) measurements in the ranges between 200-1200 nm.

All the film exhibits the absorption on the shorter wavelength. High absorbance value shows on the Zn:CuS. The curve shows a decay of absorbance with longer wavelength and also progressive increase in absorbance. The transmittance spectra show that as-deposited films are highly transmitted than the Zn:CuS thin film at visible region. The higher transmittance indicates the surface and relatively good homogeneity of the thinner film.
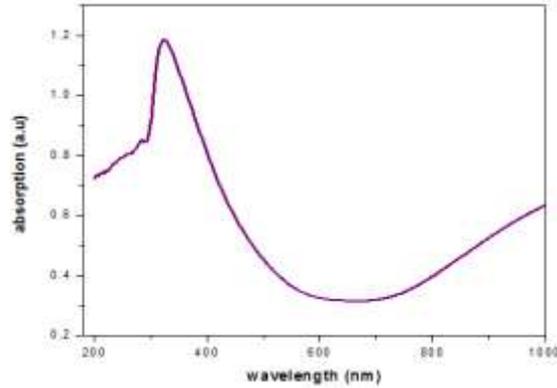

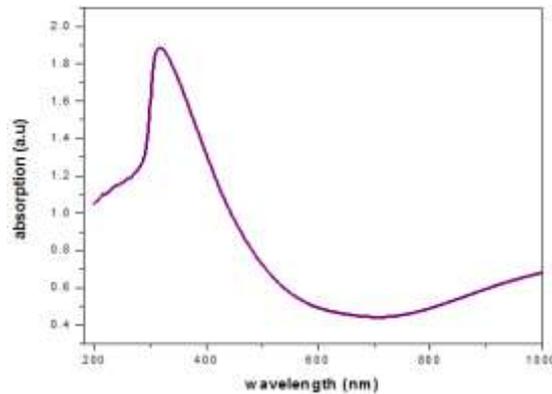**Fig. 3** Wavelength vs Absorbance of CuS thin film.

Fig. 4 Wavelength vs Absorbance of Zinc doped CuS thin film

The bandgap have been determined from the intercept of straight line portion of ($\alpha h\vartheta$)^2 versus (hϑ) and for different value of CuS and Zinc doped CuS thin films. Extrapolating the straight line portion of the plot of ($\alpha h\vartheta$)^2 against (hϑ) to energy axis for zero absorption coefficient ($\alpha = 0$) gives optical bandgap energy.

It is found that the bandgap of the CuS and Zinc doped CuS thin film samples are 1.49 and 1.43 eV respectively. The as deposited thin film shows increase in the bandgap value and Zinc doped CuS films shows decrease in bandgap value. The bandgap arises due to following reason (i) large density of dislocation (ii) height of the crystalline films. The decrease in bandgap is caused due to the increase in the height of the crystalline films. The energy bandgap shows that these films can be used as potential absorbers in solid state solar cells.
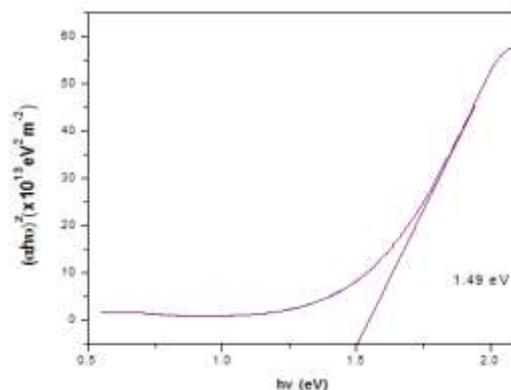

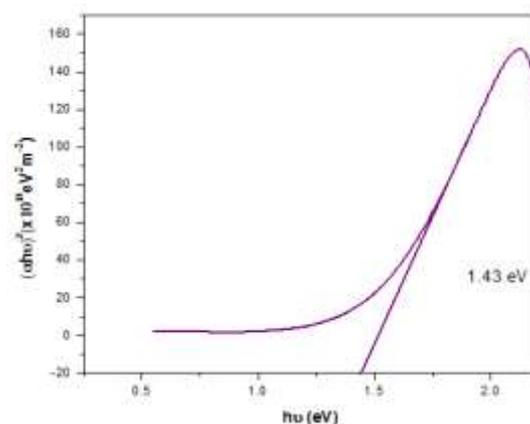**Fig. 5** plot of ($\alpha h\vartheta$)^2 vs (hυ) for CuS thin films

Fig. 6 Plot of ($\alpha h\vartheta$)^2 Vs (hυ) for Zinc doped CuS thin film

IV. Conclusion

CuS and Zinc doped Copper Sulfide thin films were deposited on glass substrates using chemical bath deposition technique at molar concentration of 0.5 M. This method is found to be simple and cost effective as the UV analysis shows high absorption value for Zn doped CuS thin films. Zn doped with CuS films shows reduction in band gap compared to the deposited films. As a result, from this analysis it is obvious that this material can be used as an effective material for solar cell application.

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