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Preparation and Thickness Measurement of $Cu_x Zn_{1-x} S$ Nanocomposite Thin Film by SILAR Method

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Abstract: *Thin film are of particular interest for fabrication of large area arise like solar cells, photo conductors, photo thermal solar coding etc, and it can be prepared by various techniques such as sputtering, CVD, CBD etc. In the present study $Cu_x Zn_{1-x}S$ nanocomposite thin films were prepared by Successive Ionic Layer Adsorption and Reaction (SILAR) method for various value of x viz 0.2, 0.4, 0.6 and 0.8. The prepared films were characterized by EDS and PXRD. The composition of the nanocomposite was estimated from the EDS data and the particle size was determined by PXRD data. The thickness of the film was calculated from weight method. The EDS and PXRD data shows that the film prepared in the present study are nanocomposites.*
Keywords*: Thin film, nanocomposite, SILAR, CuS, ZnS, Thickness.*

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I. Introduction

Copper sulfide is an important semiconductor material and has received a great deal of attention due to its unique physical and chemical properties. Zinc Sulfide (ZnS) Nanoparticles have recently received significant attention because of their unique optical, electrical and magnetic properties [1]. In recent years, thin films of CuS have attracted much attention for the Photovoltaic application due to high absorption coefficient [2, 3]**.** Mixed crystal are found to be more useful than end members crystal. Armingston *et al* [4] discussed two methods of improving the hardness of crystal are Solid solution hardening and Impurity hardening. In this view CuS and ZnS have been mixed together in the composition Cu_xZn_{1-x} S to enhance the properties of both CuS and ZnS film.

II. Materials And Methods

In the present study nanocomposite thin film of CuS and ZnS have been prepared in the composition $Cu_xZn_{1-x}S$, where x takes values x= 0.2, 0 .4 , 0.6 and 0.8 by SILAR method.

The SILAR method is basically a two-step chemical bath deposition technique in which a substrate is dipped in cationic and anionic precursors. The technique is thus based on the absorption and reaction of the ions from the solutions. Sequential reaction on the substrate surface under optimized condition of concentration and pH of the reacting solutions results in the formation of the film.

The cationic precursor for ZnS was 0.1M ZnSO4 solution which was complexed with mixture of hydrazine, hydrate and ammonia. This complexed solution of $ZnSO_4$ was stirred for 5 minutes, thiourea with concentration 0.1M was used as anionic precursor for the deposition of ZnS thin film. In this present study for the preparation of CuS film, CuS was synthesized from AR grade Copper Sulphate and thiourea by the following reactions.

$CuSO_4 \rightarrow Cu^{2+} + SO_4^-$
$CS(NH_2)_2 + 2OH^- \rightarrow S^{2-} + H_2CN_2 + 2H_2O$
$Ca^{2+} + S^{2-} \rightarrow CuS$

The above similar procedure was used for the preparation of ZnS thin film from AR grade Zinc Sulphate and thiourea by the following reaction.

$ZnSO_4 \rightarrow Zn^{2+} + SO_4^-$
$CS(NH_2)_2 + 2OH^- \rightarrow S^{2-} + H_2CN_2 + 2H_2O$
$Zn^{2+} + S^{2-} \rightarrow ZnS$

For the preparation$Cu_x Zn_{1-x}$ S nanocomposite thin film, $Cu_xZn_{1-x}S$ was synthesised from 0.1M mixed solution of $(CuSO_4)_x$ and $(ZnSO_4)_{1-x}$ where x takes values 0.2, 0.4,0.6 and 0.8 by the following reaction

$(CuSO_4)_x + (ZnS0_4)_{1-x} \rightarrow XCu^{2+} + (1-x)Zn^{2+} + SO_4^-$
$CS(NH_2)_2 + 2OH^- \rightarrow S^{2-} + H_2CN_2 + 2H_2O$
$XCu^{2+} + (1-X)\ Zn^{2+} + S^{2-} \rightarrow Cu_xZn_{1-x}\ S$

The cationic precursors for CuS, ZnS and $Cu_xZn_{1-x}S$, were 0.1M $CuSO_4$, $ZnSO_4$ and $(CuSO_4)_x.(ZnSO_4)_{1-x}$ respectively and anionic precursors used for the deposition of the film was 0.1M thiourea the p^H of the cationic solution was maintained at p^H=12 for all the cases.

Glass substrate was used for the preparation of the film in the present study. The glass substrate was cleaned, before deposition in the soap solution followed by distilled water rinse and ultrasonic cleaning with acetone and alcohol. The pre-cleaned substrate was first immersed in the cationic solution for 20second followed by immersed in the distilled water for the same time for removing the excess ion and then the substrate was immersed in the anionic solution (thiourea) which was maintained at 70^0 C for 20second and then immersed in the distilled water. The above cycle was repeated for different times viz. 30, 40, 50, and 60 totally, 24 films were prepared in the present work.

The composition of nanocomposite films were estimated from EDS spectrum and SEM picture were taken by using FEI Quanta FEG 200 Model scanning electron microscope.

The thickness of the film was measured by using weight method, which depends on the difference between weight of substrate before and after deposition of the film.

PXRD data were collected for all the samples by using XPERT-PRO Diffractometer. The grain size was estimated by using the Scherrer's formula [5]

$D= K \lambda/(\beta (COS\theta)$

Where, K is a constant(0.94), λ is the x-ray radiation used (λ=1.5406 A^0),β is the FWHM intensity in radians, θ is the Bragg's angle.

III. Results And Discussion

The EDS spectrum of the sample $Cu_{0.2}Zn_{0.8}S$ of 50 cycles is shown in figure (i). The SEM picture of the sample $Cu_{0.2}Zn_{0.8}S$ of 50 cycles is shown in figure(ii). The estimated composition of the nanocomposite calculated from EDS data along with the actual composition taken is provided in Table-I. It is found that the composition estimated for the composite well agreed with the actual composition taken for the preparation of the sample. It reveals that the nanocomposite film prepared in the present study is completely miscible.

The XRD pattern of all the samples of 50 cycles are shown figure(iii). The indexed X-ray diffraction data shows that the nanocomposites $Cu_xZn_{1-x}S$ prepared in the present study belongs to Hexagonal system. The least square average particle size determined from the XRD data and the thickness of the film prepared for different SILAR Cycles is provided in Table-II. It is found that the film prepared in the present study is a nanocomposite. The particle size of the $Cu_{0.2}$ $Zn_{0.8}S$ is even less than that of two end members (CuS and ZnS). The particle size is minimium (23.11) of $Cu_{0.2}Zn_{0.8}S$ nanocomposite and it reveals that at higher concentration of Zn, the particle size does not change. The particle size of the composites are found to vary non-linearly with the composition. The non-linear variation may be attribute to the unharmonicity due to the mixing.

The variation of the film thickness with the number of cycles are shown in Figure(iv). It is found that thickness of the film increases with increase in number of cycles and it reaches maximum at 60 cycles. It decreases with increase in Cu ion composition.

Table-I Weight Percentage and Estimated Composition of all the samples of 50 cycles

S.NO	System	Weigh Percentage(Atomic%)		Estimated Composition
		copper	zinc	
1.	CuS	---	---	---
2.	$Cu_{0.2}$ $Zn_{0.8}S$	3.82	17.45	$Cu_{0.18}$ $Zn_{0.82}S$
3.	$Cu_{0.4}$ $Zn_{0.6}S$	7.19	8.77	$Cu_{0.44}$ $Zn_{0.56}S$
4.	$Cu_{0.6}$ $Zn_{0.4}S$	29.45	17.56	$Cu_{0.63}$ $Zn_{0.37}S$
5.	$Cu_{0.8}Zn_{0.2}S$	18.26	0.96	$Cu_{0.82}$ $Zn_{0.18}S$
6.	ZnS	---	---	---

Table –II Thickness for all cycles, density and particle size for all the sample of 50 cycles

S.N0	System	Densiy	Thickness				Particle size
			30 cycles	40 cycles	50 cycles	60 cycles	
1.	***CuS***	***4.6000***	***8.6957***	***10.1449***	***11.5942***	***13.0434***	**69.33**
2.	**$Cu_{0.2}Zn_{0.8}S$**	**4.1818**	**9.5419**	**11.1323**	**12.7537**	**14.3129**	**23.11**
3.	**$Cu_{0.4}Zn_{0.6}S$**	**4.3144**	**9.3153**	**10.8678**	**12.3617**	**13.9729**	**51.35**
4.	**$Cu_{0.6}Zn_{0.4}S$**	**4.4113**	**9.0991**	**10.6157**	**12.0901**	**13.6488**	**27.73**
5.	**$Cu_{0.8}Zn_{0.2}S$**	**4.5082**	**8.8928**	**10.3749**	**11.8302**	**13.3392**	**53.33**
6.	**ZnS**	**4.0900**	**9.7799**	**11.4099**	**13.0399**	**14.6699**	**69.33**

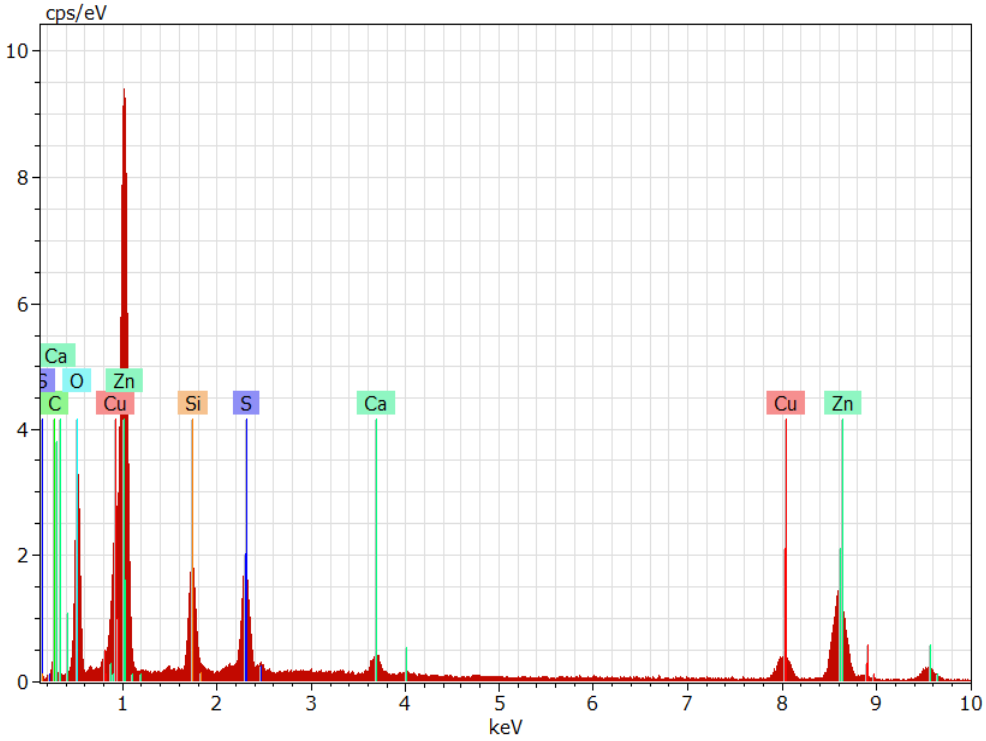

Fig (i)EDS Spectrum of $Cu_{0.2}Zn_{0.8}S$ thin film of 50 cycles

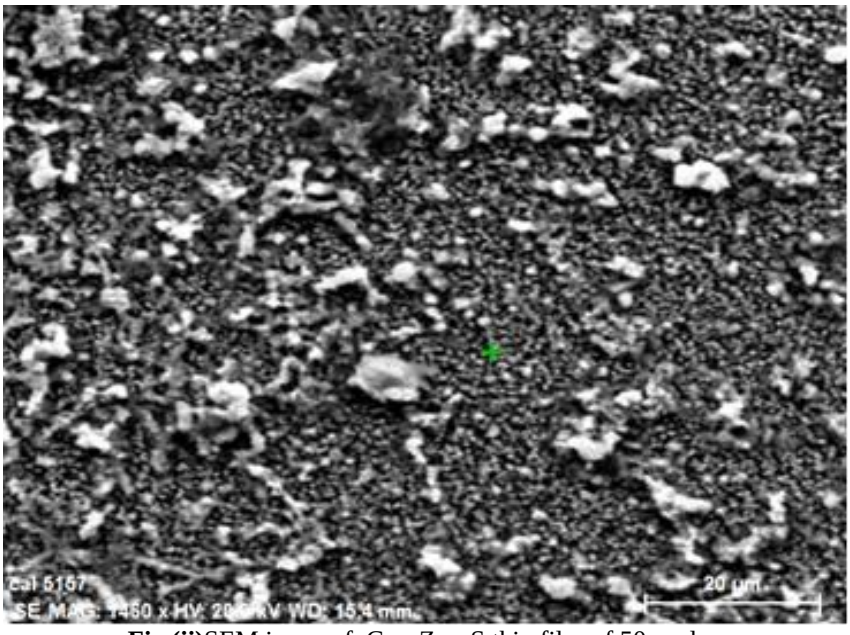

Fig (ii)SEM imageof $Cu_{0.2}Zn_{0.8}S$ thin film of 50 cycles

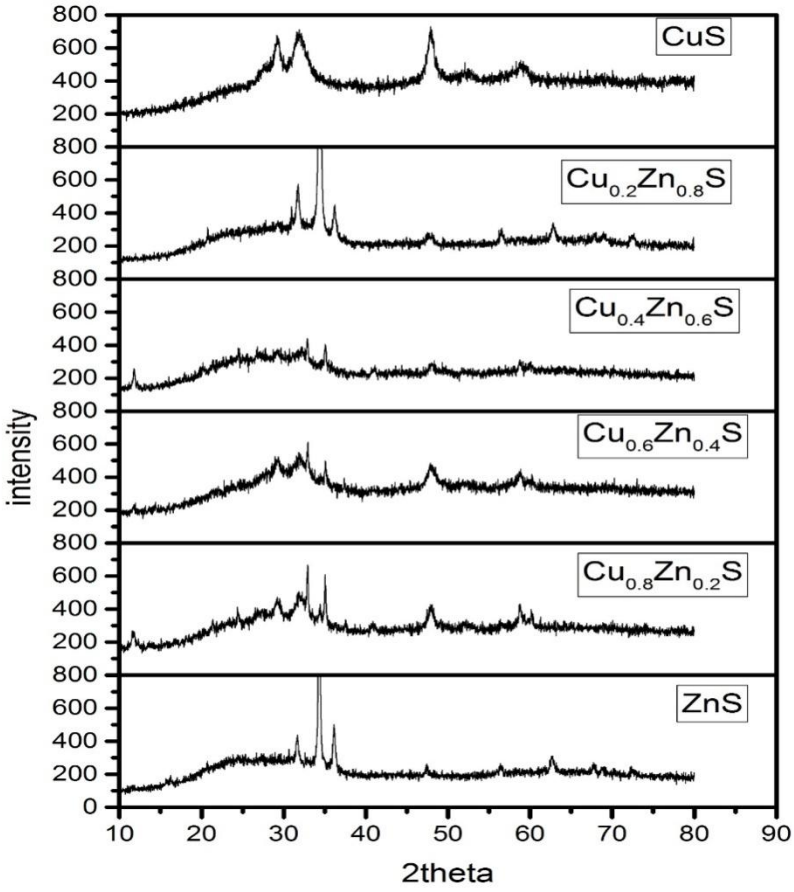

Fig (iii)XRD Pattern of all the samples of 50 Cycles

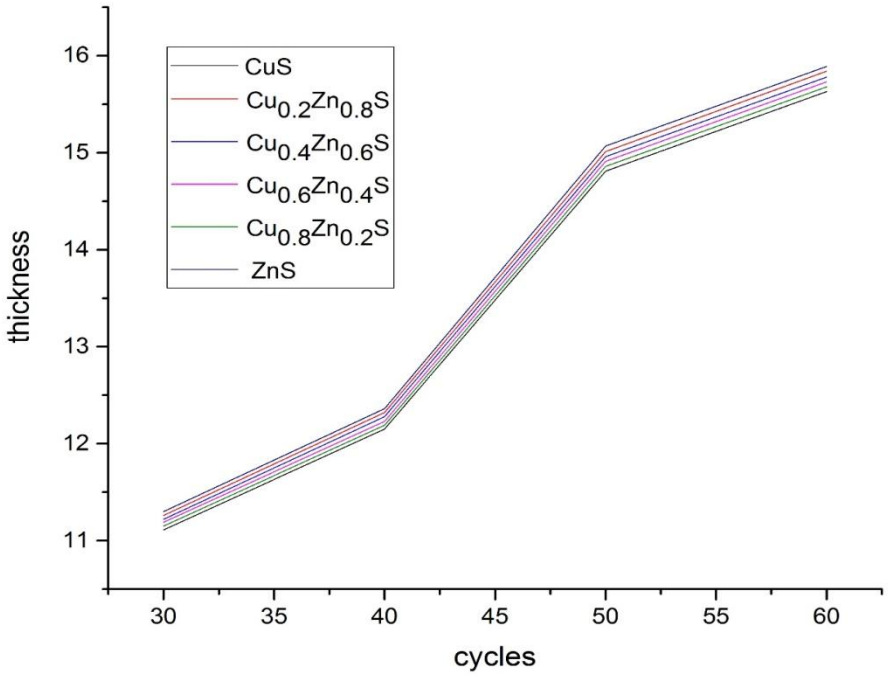

Fig (iv) Variation of thickness with SILAR Cycles for all the samples of 50 Cycles

IV. Conculsion

The particle size and estimated composition of the mixed crystals shows that it is a nanocomposite. The nanocomposites prepared in the present study belong to Hexagonal System. The thickness of the film increases with increase in number of cycles and it decreases with increase in Cu ion composition.

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