

Thickness Dependent Physical Properties of SILAR Deposited Nanostructured CoS Thin Films

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The preparation of nanostructured CoS thin films onto amorphous glass substrate by SILAR method is discussed. The characterization techniques such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Optical absorption and Electrical resistivity measurements were used to investigate size dependent physical properties of CoS thin films. The SILAR grown CoS material exhibits hexagonal structure . The electrical studies revealed that the resistivity and activation energy is found to be thickness dependent. The thermo-emf measurements confirmed that SILAR grown CoS films are of n-type.

Keywords: Thin film; CoS; SILAR method; Electrical properties

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1. Introduction

Thin film is a microstructure, that is formed by the atomic/molecular layers of a material deposited at the surface of a solid (bulk) material and its one of the dimensions is much smaller than the other two. Thin films metal sulphides, both crystalline and amorphous are very important in the modern technology. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are: microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, A. R. coating, photoconductors, IR detectors, interference filters, solar cells, polarisers, temperature controller in satellite, super conducting films, anticorrosive and decorative coatings.¹² From last two decades, nanocrystalline thin films of metal sulphides grown by chemical route have been extensively studied due to their commercial outstanding applications in optoelectronic devices. The fabrication of nanocrystalline thin films in unlimited quantities with outstanding fundamental and potential technological consequences is the ultimate challenge of modern materials research. Thin film products are utilized in many applications in modern day. Interestingly it has been observed that, the chalcogenide thin films show outstanding activity for variety of applications such as Solar Cell, Gas Sensor, magnetic storage devices, super capacitor and electro catalysts.3-10 Amongst various chalcogenides CoS has particular interest due to its novel physical and chemical properties." It is one of the most complicated system known due to its number of phases such as CoS, Co₃S₄, CoS₂, Co₉S₈, etc.¹² Basu et al.¹³ prepared CoS films using chemical bath deposition with thioacetamide as the sulfur source. Synthesis of cobalt sulphide thin films is made possible in an aqueous alkaline medium (pH = 11) using liquid phase chemical deposition process.¹⁴ M. A. Sattar et al reported preparation of cobalt sulfide thin

¹Nanostructured Thin Film Material Laboratory, Department of Physics, Govt. Vidarbha Institute of Science and Humanities, VMV Road, Amravati 444604, Maharashtra, India ***E-mail:** ashokuu@yahoo.com films by spray pyrolysis method at constant substrate temperature 300 °C.¹⁵ Recently, synthesis of CoS thin films was carried out by a modified liquid phase chemical growth process.¹⁶⁻¹⁷ However, their deposition process is complicated and difficult to control. Very few reports are available on growth of CoS thin films by physical and chemical route. In this paper, we have outlined our efforts to deposit semiconducting nanostructured CoS thin films by SILAR method. In addition, the effect of film thickness on various physical properties of CoS is discussed.

2. Experimental

In SILAR method, to grow nanocrystalline thin film the substrate is immersed repeatedly into separately placed cationic and anionic precursor alternately.¹⁸ To remove loosely bound species, after each precursor immersion, the substrate is rinsed in de-ionized water.¹⁹⁻²² For the present work the glass micro slides of size 75×25×2 mm were used as substrates. Before actual deposition cleaning of the substrate is very important as it affects the growth mechanism. Initially, the slides were washed with liquid detergent, then boiled in concentrated chromic acid for 2 hour, and then kept in it for next 48 hours. The substrates were then washed with double distilled water and cleaned in ultrasonic cleaner for 10 min. Finally, the substrates were dried using AR grade acetone and kept in dust free storage container.23 For deposition of CoS thin films 0.05 M cobaltous sulphate and of 0.01 M sodium sulphide were used as cationic and anionic precursors. The well cleaned glass substrate was then immersed in a cationic precursor for 20 S, where cobalt ionic species were adsorbed. This substrate was then rinsed in de-ionized water for 20 S to remove loosely bound species of Co²⁺ ions from the substrate surface. After removal of loosely bound species of Co²⁺ the substrate was then immersed in an anionic precursor for 10 S to form a layer of CoS material. To remove unreacted or excess species from substrate surface again, it was rinsed in deionized water for 20 S. Complete SILAR deposition is schematically shown in Fig. 1. In SILAR method glass substrate is immersed alternately into separately placed cationic and anionic precursors. which gives ion - by - ion growth mechanism at nucleation sites on the immersed surfaces.²⁴ A

well-cleaned glass substrate was immersed in $CoSO_4$ cationic precursor solution where Co^{2^+} ions were adsorbed on the surface of the substrate [Co (OH)₂ adsorption is neglected]. The substrate was then rinsed in ion exchange water, to remove loosely bounded Co^{2^+} ions. After rinsing, substrate was immersed in Na₂S anionic precursor solution. Where HS', S², OH and Na⁺ ions were diffused from the solution in the diffusion layer towards solid solution interface until their concentration in the diffusion equals those in bath. The immersion time is experimentally calculated. The HS' and S²⁻ enter into the outer Helmholtz layer and reacts with the adsorbed Co^{2^+} to form monolayer of CoS. This completes one deposition cycle. The overall reaction can be written as,

$$\operatorname{Co}_{aq}^{2+} + \operatorname{So}_{4aq}^{2-} + 2\operatorname{Na}_{aq}^{+} + \operatorname{So}_{2aq}^{2-} \longrightarrow \operatorname{CoS} + 2\operatorname{Na}_{aq}^{+} + \operatorname{SO}_{4aq}^{2-}$$
(4)

It is observed that for 35 SILAR Cycles CoS film has thickness 201 nm and it increases to 513 nm up to 75 cycles. Above 75 cycles film surface shows peel off character may be due to strain between excess mass of deposited material with substrate and hence thickness decreases to 275 nm for 115 cycles (Table 2). The average growth rate of CoS for first 35 cycles was found to be 5.75 nm/cycles and it becomes maximum 6.8 nm/cycles for 75 cycles and then decreases. This supports the fact that, in the beginning the concentration of cation



Fig. 1 The scheme of SILAR method for the deposition of thin films.

Deposition Parameters	Cationic Precursor	Anionic Precursor
Precursor	CoSO ₄	Na ₂ S
Concentration (M)	0.05	0.01
pH	4	12
Immersion time (S)	20	10
Rinsing Time (S)	20	20
Volume of Precursor (mL)	80	80
Temperature (K)	303	303

Table 1 Optimized deposition parameters for CoS this	nin films.
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 Table 2 Variation of growth rate and thickness with SILAR cycles.

Thickness (nm)	Growth rate nm/cycles
201	5.74
262	4.76
513	6.84
413	4.34
275	2.39
	Thickness (nm) 201 262 513 413 275

and anion is maximum and it decreases with number of cycles.²⁵

The color of as grown CoS film has changed from grayish black to dark black colour as deposition cycles were increased from 35 to 115. After 95 cycles film starts to peel off into rinsing solution. In order to deposit good quality adhesive CoS films several deposition trials were carried out. The optimized preparative parameters for the synthesis of CoS thin films are tabulated in Table 1.

In the present work, thickness of the film was measured by gravimetric weight difference method using the relation,

$$t = m/\rho * A \tag{1}$$

where 'm' is the mass of the film deposited on the substrate in gm. 'A' is the area of the deposited film in cm² and ρ is the density of the CoS in bulk form.

The crystal structure of the deposited film was identified by normal and grazing incidence X-ray diffraction analysis with X-ray diffractometer (Regaku Miniflex 600) with CuK α radiation of wavelength 0.154 nm. Surface morphological analyses of CoS thin films deposited on glass substrates were performed using FE-SEM (JEOL JSM-7500F). The variation of electrical resistivity with temperature was measured using two-point probe technique with digital electrometer and a stabilized power supply. Optical absorption studies were carried out using a UV–Vis spectrophotometer (UV-1800) in the wavelength range 350–950 nm.. The nature of the transition (direct or indirect) is determined via the relation,

$$\alpha = (hv - Eg)^n / hv \tag{2}$$

where *hv* is the photon energy, *Eg* is the band gap energy, and *A* and *n* are constants. For allowed direct transitions n = 1/2; for allowed indirect transitions n = 2.

The DC two point probe method was employed to understand the

variation of electrical resistivity of CoS with temperature. The thermal activation energy ${\rm 'E_a'}$ was calculated by using relation,

$$\rho = \rho_{o} \exp\left(-Ea/KT\right) \tag{3}$$

where $\rho_{\rm o}$ is a parameter depending on the sample characteristics (thickness, structure etc.), $E_{\rm a}$ denotes the thermal activation energy of electrical conduction, K is Boltzmann's constant and T is absolute temperature. The thermoelectric power measurements were used to determine the type of conductivity. The temperature difference between the two ends of the sample causes transport of carriers from the hot to cold end, thus creating an electric field, which shows thermo-emf across the.²⁶

The XRD patterns of the CoS films of various thicknesses deposited on glass substrates are shown in Fig. 2. Table 3 summarizes the crystallographic data of these films compared with standard JCPDS data file CoS: 75-0605. The analysis showed that the films are nano crystalline in nature with hexagonal structure. The (100), (002), (101) and (102), (110), (201), (200), (112) and (004) XRD peaks confirms hexagonal structure of CoS in accordance with JCPDS card (Table 3). These results are in good agreement with the literature reported earlier.²⁷ The average crystallite size of the film material was determined by using Debye - Scherrer formula.²⁸

$$D = K\lambda / \beta Cos\theta \tag{5}$$

where λ is the wavelength used (0.154 nm), K is constant, β is the angular line width at half maximum intensity in radians; θ is the Bragg's angle. The crystallite size of CoS increases with film thickness. (Table 4).

The SEM micrographs of CoS films having different thicknesses are shown in Fig. 3. It is observed that the CoS thin films are uniform, homogeneous and well covered to the glass substrate. The nano sized grains are uniformly distributed over the homogenous background and



Fig. 2 XRD Patterns of CoS films.

shows improvement in crystallinity with thickness. Also as thickness increases, the agglomeration of grains at some places is observed on homogeneous background. The remarkable agglomerated overgrowth is observed above 262 nm film thickness and becomes maximum at 513 nm. At higher thickness this agglomerated overgrown material starts to detach from the surface in turn that decreases the surface roughness.

The variation of optical absorption αt with wavelength λ is shown

in Fig. 4. It is observed that absorption coefficient of CoS thin film increases as thickness increases. Also towards shorter wavelength higher absorption is observed. The plots of $(\alpha hv)^2$ versus hv are shown in (Fig. 5) for CoS films of various thicknesses. The optical band gap energy is estimated by extrapolating the straight part of $(\alpha hv)^2$ line to hv axis. The optical band gap energy of CoS decreases from 2.01 to 1.72 eV as thickness increases from 201 to 513 nm (Table 4) this is because; the

Tuble 5 comparison of observed and standard Arth data of cos and mins. (Set D5 cards .75 0005 of cos)				
Film thickness	Standard 20 (degree)	Observed 20 value (degree)	hkl	
A (201 nm)	30.607	30.454	100	
	34.883	34.434	002	
	54.407	54.407	110	
	73.662	73.752	004	
	20 (07	20 (72	100	
B (262 nm)	30.607	30.003	100	
	34.457	34.883	002	
	54.583	54.407	110	
C_{1} (513 nm)	66 560	66.068	112	
C (515 mil)	20,607	20.826	100	
	30.007	30.820	100	
	34.883	34.454	002	
	35.338	35.427	101	
	47.078	47.400	102	
	54.407	54.170	110	
D (413 nm)	63.724	63.333	200	
	66.275	66.380	112	
	30.607	30.393	100	
	34.883	34.008	002	
E (275 nm)	35.338	35.305	101	
	47.078	47.427	102	
	54.407	53.529	110	
	30.607	30.380	100	
	34.683	34.312	002	

 Table 3 Comparison of observed and standard XRD data of CoS thin films. (JCPDS Cards :75- 0605 of CoS)

Table 4 Variation of grain size with film thickness of CoS.

Thickness (nm)	Crystallite Size (nm)
201	27
262	32
513	64
413	46
275	40

bulk material does not have discrete energy states. But as the particle become smaller, the energy levels become discrete.²⁹ According to particle in box concept, energy gap between different energy states is inversely proportional to the square of the length of the box, for quantum dot, the length of the box is actually its size. So with decrease in size, the energy gap increases. This is primary reason behind dependence of band gap energy of nano crystalline thin films.

To study electrical properties, the DC two point probe method has been employed. From the resistivity measurements it was observed that the resistivity of CoS decreases with increase in temperature indicating its semiconducting behavior. Fig. 6 shows the variation of log of resistivity (log ρ) with reciprocal of temperature (1/T)*10³ For CoS films the activation energy was estimated from resistivity plots The value of activation energy in lower region decreases from 0.18 to 0.15 eV as film thickness increases from 201 nm to 513 nm, as film stats to

peel of above 513 nm thickness activation energy also increases and exact opposite behavior was observed in higher temperature region. It increases from 0.63 to 0.70 eV as film thickness increase from 201 to 513 nm and decreases to 0.66 eV as thickness decreases to 275 nm.

In order to investigate the type of conductivity of CoS, the thermo-emf developed by applying temperature gradient across the film has been measured the thermo-emf generated is directly proportional to the temperature gradient maintained across the semiconductor ends as well as to the film thickness. The type of conductivity was decided from the sign of the emf generated at the cold and hot end. In this case the negative terminal was found to be at the cool end; therefore, the film shows n-type conduction mechanism. It was observed that, as the film thickness increases, thermo-emf developed across the film also increases, which may be due to increased carrier concentration and mobility of charge carriers in the film.³⁰





(C)





Fig. 3 SEM micrograph of CoS thin films of thickness (A) 201 nm, (B) 262 nm, (C) 513 nm, (D) 413 nm (E) 275 nm.





Fig. 4 Plots of optical absorption versus wavelength of CoS thin films.



Fig. 5 Plots of $(\alpha h \upsilon)^2$ Vs h υ for CoS thin films with different thickness.









3. Conclusion

Nanostructured CoS thin films were prepared onto glass substrates using simple and economic SILAR technique. The X- ray diffraction study revealed that the films are nanocrystalline in nature with hexagonal structure. Electrical resistivity measurements indicate semiconducting nature of CoS thin films. The activation energy and optical band gap of CoS decreases with increase in thickness, which may be due to different size effects.In conclusion it was observed that physical properties of CoS can be engineered by adjusting film thickness.

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