

Investigation on Cobalt sulphide thin films: Growth Mechanism, Structural Analysis and Optical Properties

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Abstract— Cobalt sulphide thin films were deposited using the most simple and inexpensive Chemical bath deposition method. The CoS thin films were deposited on glass substrates using aqueous alkaline medium consisting NH₃ and TEA as the complexing agents, in presence of Cobalt sulphate and Thiourea as Co²⁺ and S²⁻ ion sources respectively. The deposition was done under pre-optimized conditions such as temperature 60 ± 0.5^o C, deposition time 90 minutes, speed of rotation of substrate solution 70 ± 2 rpm. The quantity of NH₃ and concentration of TEA in the reaction mixture were the key factors controlling the deposition of the thin film. The films so obtained were peacock green in colour, uniform and highly adherent in nature. The films were polycrystalline with hexagonal crystal structure. The absorption coefficient of the film was found to be very high ($\alpha \approx 10^4 \text{ cm}^{-1}$) over a wide range of visible spectrum. The optical band gap energy ($E_g = 1.65 \text{ eV}$) was estimated from the plot of $(\alpha h\nu)^2$ versus $h\nu$ (direct allowed transition) and ($E_g = 1.65 \text{ eV}$) from the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (indirect allowed transition). The broad absorption edge in the visible region of the spectrum with very high absorption coefficient suggests that CoS material is a very good candidate for photovoltaic and optoelectronic applications.

Keywords- Cobalt sulphide, Chemical bath deposition, XRD, Optical band gap.

I. INTRODUCTION

Cobalt sulphides form a group of II-VI semiconductor materials that are attracting a considerable attention in recent years, although they are complicated metal chalcogenides. II – VI and IV-VI group chalcogenides are classified as direct band gap semiconductor with as sharp optical absorption edge and large absorption coefficients [1,2]. Consequently, semiconductor thin films of II-VI and IV-VI groups, are of great interest due to their unique physical and electro-optic properties and their potential applications in variety of optoelectronic devices such as in photoconductors, radiation detectors, DMS materials, light emitting diodes, lasers, thin film transistors and photoelectric cells including photoconductive and photovoltaic Solar cells [3,11-14]. Cobalt sulphide thin films are of particular interest due to their unique catalytic, electrical, optical and magnetic properties and exhibit strong intrinsic absorption in the visible and near infrared regimes of the electromagnetic spectrum [3, 11-14]. In view to gain insight into these inherent properties, several efforts have been dedicated to the synthesis of Cobalt sulphides with various morphologies such as nanoparticles, nanowires, thin films, octahedrons and recently sea-urchin phases [3, 11-14].

II. EXPERIMENTAL DETAILS.

A. Thin film deposition.

Cobalt sulphide thin film deposition was done by the Chemical bath deposition technique. Thoroughly cleaned amorphous spectroscopic glass substrates were utilized to deposit CoS material. The chemicals and solution precursors used for the preparation of CoS thin films were AR Grade

chemicals and were prepared in double distilled water. Firstly, 10 ml of 1M solutions of Cobalt sulphide and Thiourea were prepared in double distilled water. 1M Cobalt sulphate solution was added with TEA, with constant stirring to form Co²⁺ complex. Then 10ml of 1M Thiourea was added to the reaction mixture with constant stirring. Then NH₃ was added to the reaction mixture to maintain pH of the mixture between 9 to 10.5. Then double distilled water was added to the mixture to make it up to 200ml. Then clean microscopic slide was clamped vertically into the beaker by means of a specially designed slide holder. Then this beaker with 200ml reaction mixture was placed in an oil bath whose temperature was maintained constant at 60^oC. The reaction mixture was stirred at a constant speed of 70± 2 rpm for 90 mins. Then the glass slides were removed, rinsed and dried in open air. To investigate the effect of Ammonia and TEA concentration on the growth of the CoS thin film a series of sample slides were prepared by varying NH₃ and TEA concentrations separately keeping the other conditions and reagent concentrations constant. Then NH₃ = 17 ml and TEA = 2.8 ml was selected from the terminal layer thickness observations and the slide was set for deposition keeping all other conditions constant. The CoS thin film so deposited was highly uniform, strongly adherent to the glass substrate and peacock green in colour.

B. Characterization of Sample.

The optical absorption measurement was carried on the deposited thin film using UV-VIS-NIR Spectrophotometer (double beam Shimadzu-3600) in the wavelength range of 320nm to 1000nm. The structural characterization was performed by using X-ray powder diffraction method using Cu α radiation ($\lambda = 1.5406 \text{ \AA}$, 40kV, 30mA in the 2 θ range from

0° to 80°). The thickness of the film was measured by using interference technique.

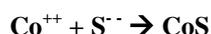
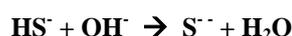
III. RESULTS AND DISCUSSION.

A. Chemical Reaction and Growth Mechanism.

The chemical reaction that occurs in the reaction mixture is as follows:-



where R = H/CH₂CH₂OH



In general, deposition of the metal chalcogenide initiates only when the concentration of the anions and cations exceeds the solubility product ($k_{sp} \text{ CoS} = 10^{-21}$) [3, 15, 17]. Excess concentration in the bath leads to supersaturation, providing the driving force and therefore favouring nucleation due to the unstable thermodynamic condition [15]. The ionic product exceeds the solubility product and precipitation occurs via heterogeneous growth reaction on the substrate. Co^{2+} and S^{2-} ions react with each other and form nuclei which either precipitate spontaneously or very slowly in highly alkaline medium. When the ionic product starts to exceed the solubility product, Cobalt sulphide nuclei are produced both on the substrate and in the solution. Thus they serve as an ideal building block and tend to assemble into the form of primary structures. This activates the nucleation of CoS layer in an aqueous alkaline environment and consequently initiates the development of thin solid deposit on to the substrate surface [15, 16].

In the first step of the above chemical reaction TEA forms a complex with Co^{2+} , reducing the release of free Co^{2+} ion concentration, resulting in reduction in the rate of growth of film. Formation of Co^{2+} – TEA complex provides the priority to the heterogeneous nucleation on the substrate. While at specific temperature $(\text{NH}_2)_2\text{CS}$ decomposes and produces S^{2-} ions for the formation of CoS. Hydrolysis of $(\text{NH}_2)_2\text{CS}$ causes Co^{2+} – TEA complex to react with S^{2-} anions, resulting in the formation of a single CoS nuclei.

B. Action of Complexing Agents.

A complexing agent is usually employed to control the reaction at suitable rate to obtain the desired thin film growth [1, 15, 16]. In the present case, NH_3 and TEA liberate OH^- ions in the solution bulk and forms complex with Co^{2+} ions. Hence, with addition of NH_3 and TEA two processes start simultaneously; (i) the complexation of Co^{2+} ions and (ii) the control of p^{H} of the resulting solution which enhances the rate of thin film layer formation. The addition of OH^- ions (increase in NH_3 quantity) makes the Co^{2+} – TEA complex more stable and metal ions are well arrested by the complexing agent which controls the rate of release of metal ion species and consequently the layer thickness [15,16]. Therefore the quantity of NH_3 and concentration of TEA were

varied one at a time and the thickness of the film so formed was measured. The effect of NH_3 quantity and TEA concentration on the growth of the film and the resulting thickness of the thin film formed can be well depicted from Fig.1. Fig.1.A. illustrates the effect of variation of quantity of Ammonia in the reaction mixture on the growth of CoS thin film. The plot shows that the thickness of the thin film deposited increases linearly with increase in quantity of Ammonia in the reaction mixture. The thickness 't', of the film formed is maximum at 17ml of Ammonia and then decreases linearly with further increase in Ammonia quantity. Similar case is observed with TEA concentration in the reaction mixture. The thickness of the film, 't', is maximum at 2.8ml of TEA concentration as shown in Fig.1.B. This observation is in close agreement with reported results [3].

Table.1.A. Effect of quantity of Ammonia on thickness of CoS film.

Sr.No.	Quantity of NH ₃ (ml)	Thickness of CoS film (nm)
1	10	414
2	14	480
3	16	516
4	17	542
5	18	444
6	19	400
7	20	390

Table.1.B. Effect of TEA concentration on thickness of CoS film.

Sr.No.	TEA concentration (ml)	Thickness of CoS film (nm)
1	2	404
2	2.4	500
3	2.6	574
4	2.8	644
5	2.9	571
6	3	520

Table.1.A. above shows variation in the thickness of the as-deposited CoS thin film when Ammonia quantity was varied from 10 ml to 20 ml.

Table.1.B. above shows the variation in thickness of CoS thin film when the concentration of TEA was varied from 2 ml to 3 ml.

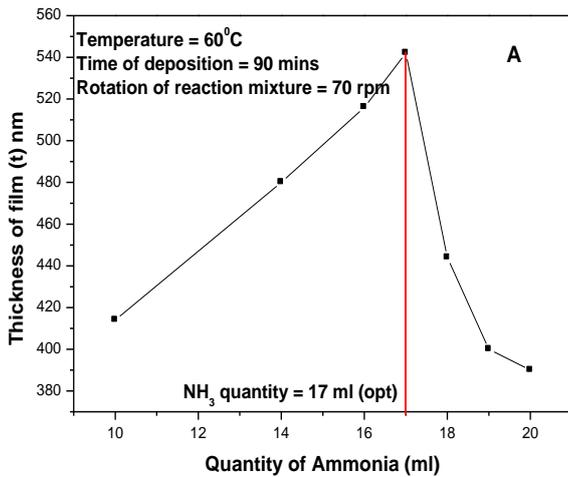


Fig.1.A. Effect of quantity of Ammonia on thickness of CoS film.

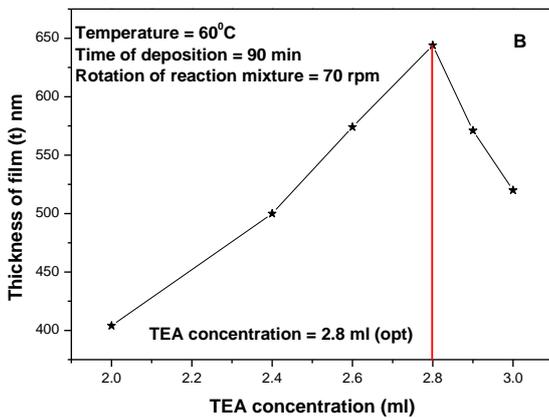


Fig.1.B. Effect of TEA concentration on thickness of CoS film.

C. XRD Analysis.

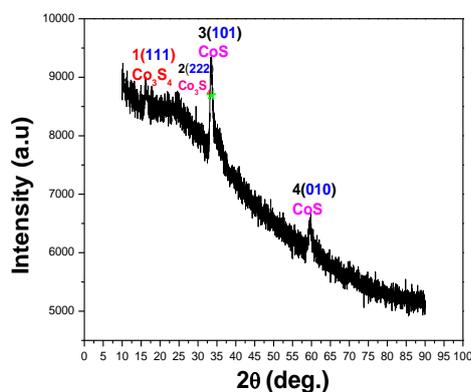


Fig.2. X-Ray diffractogram of CoS thin film

Fig.2. illustrates the recorded XRD diffractogram of CoS thin film of thickness 405 nm deposited at substrate temperature of 60⁰ C. The diffraction pattern clearly shows

that CoS thin film is polycrystalline and hexagonal in structure. The prominent peaks of CoS are observed at $2\theta = 33.48^0$ which corresponds to (101) planes with d value of 2.6743×10^{-4} cm (card no. 03-065-0407) and at $2\theta = 59.58^0$ which corresponds to (010) planes with d value of 1.5510×10^{-4} cm (PDF # 190366). The other prominent peaks correspond to Co_3S_8 , another phase of Cobalt sulphide at $2\theta = 16.26^0$ which corresponds to (111) planes with d value of 5.4468×10^{-4} cm (PDF # 110121) and at $2\theta = 31.22^0$ which corresponds to (222) planes with d value of 2.8626×10^{-4} cm (PDF# 190364). The crystal structure is a mixture of two phases, hexagonal CoS and cubic Co_3S_8 . The average crystallite size was calculated from (101) planes using Scherrer's relation,

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where, D is the average crystallite size, β is full width at half maximum of the diffraction line, θ is diffraction angle, and λ is the wavelength of the X-ray radiation. The size of the crystallite was estimated to be 47 nm. The presence of broad crystal diffraction peaks indicate that the thin film deposited on the substrate is of nano-size [18, 19]. Nanocrystalline thin films are of significant interest for a large variety of electronic and optoelectronic devices [20, 21]. Table.2.. shows the observed values of lattice parameters, intensities of reflections and d-values which are in perfect agreement with the JCPD card No. 03-065-0407, PDF # 190366, PDF# 110121, PDF# 190364 respectively.

Table.2. Structural parameters of CoS thin films deposited at optimised conditions of

TEA concentration = 2.8ml, NH_3 quantity = 17ml

20	20	d-spacing in (Å) observe	d-spacing in (Å) standard	I/I _{max} _x	I/I _{max}	Phase	Phase
Obs.	Std.			Obs.	Std.	CoS	Co ₃ S ₈
Deg.	Deg.					Hexagonal	Cubic
16.26	16.19	5.4468	5.47	97	20	----	-111
31.22	31.18	2.8626	2.866	87	5	----	-222
33.48	33.81	2.6743	2.679	100	4.8	-101	----
59.58	59.55	1.5504	1.551	72	2	-10	-----

IV. OPTICAL STUDIES.

A. Transmission characteristics.

The transmission spectrum of as-deposited CoS thin film in the UV-Visible region is illustrated in Fig.3. The transmission spectrum shows that the CoS thin film has very

low transmission coefficient in the UV-visible range which linearly increases in the IR wavelength region.

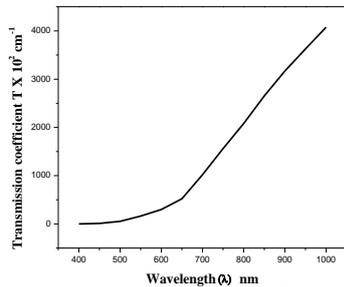


Fig.3. Variation of Transmission coefficient with Wavelength for CoS thin films.

B. Absorption characteristics.

The absorption coefficient as expected was found to be very high ($\alpha \approx 10^4 \text{ cm}^{-1}$) in the visible region of the spectrum which linearly decreased in the IR wavelength region as illustrated in Fig.4.

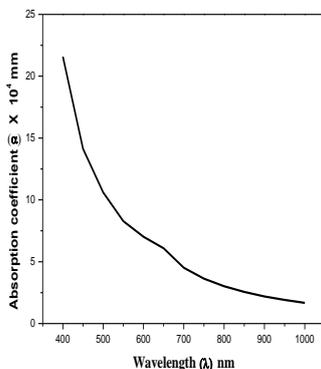


Fig.4. Variation of Absorption coefficient with wavelength for CoS thin film.

B. Optical Band gap.

To investigate optical Band gap and evaluate the band gap energy a plot of $(\alpha h\nu)^2$ Vs $h\nu$ (direct allowed transition) as shown in Fig.5.A. and a plot of $(\alpha h\nu)^{1/2}$ Vs $h\nu$ (indirect allowed transition) as shown in Fig.5.B. were plotted. The band gap energy was obtained from the intercept on the energy axis after extrapolation of the straight line section of the plots as shown in Fig.5. below.

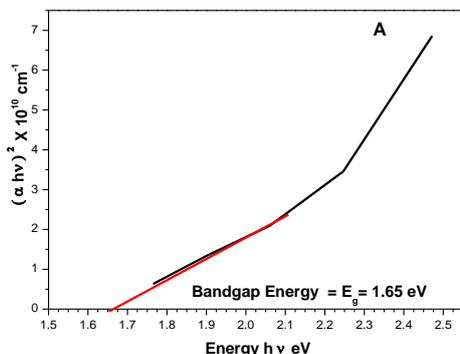


Fig.5.A Variation of Absorption coefficient for CoS thin films.

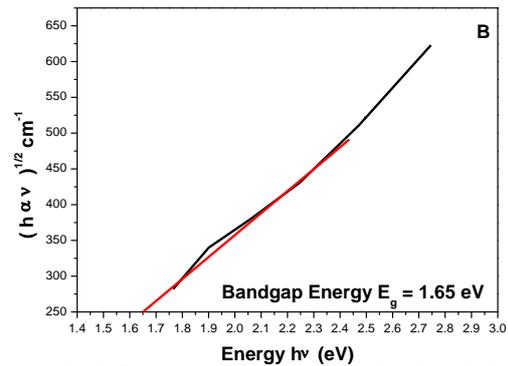


Fig.5. B Variation of Absorption coefficient for CoS thin films.)

The optical band gap energy of the as-deposited CoS thin film was $E_g = 1.65 \text{ eV}$ (direct transition) agree well with the reported values [16]. It was also seen that the optical band gap energy $E_g = 1.65 \text{ eV}$ (indirect transition) may be for Co_3S_8 . From the nature of the graph (Fig.5.A) it may be predicted that the as-deposited CoS thin films are direct band gap semiconductor. The optical investigations make it clear that Cobalt sulphide films have mixed phases of CoS with Co_3S_8 .

V. CONCLUSIONS.

Cobalt sulphide thin films were deposited by Chemical bath deposition technique. XRD analysis shows that the films are polycrystalline with hexagonal crystal structure. The optical studies reveal that Cobalt sulphide thin films are direct band gap semiconductor. The absorption coefficient of the CoS thin film was found to be very high ($\alpha \approx 10^4 \text{ cm}^{-1}$) in the visible region of the spectrum. The optical band gap energy was found to be $E_g = 1.65 \text{ eV}$. These observed characteristics of the as-deposited CoS thin films make them very good materials for photovoltaic and optoelectronic applications.

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