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Growth Mechanism, Structural Analysis and Optical Properties of CoS Thin Film

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Abstract— Cobalt Sulphide thin films, nanocrystalline in nature were deposited by using the most simple and efficient Chemical bath deposition method. In this process of deposition of CoS thin film Cobalt sulphate was used as Co^{+2} and Thiourea as S^{-2} ion sources. The X-ray diffraction observations showed that the thin films were nanocrystalline with hexagonal structure. The observed d-values and lattice parameters perfectly matched with the standard values. The average crystallite size determined using Scherrer's relation was found to be in the nano range i.e. 47 nm. The optical measurements were carried out on the deposited thin film using US-VIS-NIR Spectrophotometer UV-3600. The UV-VIS absorption spectrum of CoS thin film illustrates that the films are good absorbers in UV region, very poor absorbers in IR region & moderate absorbers in the visible region of the spectrum. The absorption coefficient of the as-deposited CoS thin film is found to be high of the order < 10^4 and the Bandgap energy to be E_g = 1.6 eV. The plot of $(\alpha h\nu)^2$ against (hν) verifies that the CoS thin film is a direct Band gap semiconductor. The band gap energy was found to be E_g = 1.62 eV from the plot of $(\alpha h\nu)^{1/2}$ against (hν) The UV- VIS transmission spectrum of CoS film illustrates highest transmission in IR region, lower in visible and lowest in UV region of the spectrum.

Keywords- *Cobalt sulphide, Chemical bath deposition , X-Ray diffraction , Nanocrystalline thin films, Optical band gap.*

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I. INTRODUCTION

Nanocrystalline Cobalt Sulphide thin films evoked much attention due to their vast potential uses in various field. Cobalt Sulphide has wide range of well perspective applications in solar selective coatings, IR detectors and as a storage electrode in photoelectrochemical storage device. There are different phases of CoS, the phase Co_3S_4(which occurs naturally as linnaeite) is stable up to about 650°C; thereafter CoS_2 and $Co_{1-X}S$ are formed. The phase Co_9S_8 is peritectically formed around 835°C [1, 2]. Recently, synthesis of CoS thin films was carried out by a modified liquid phase chemical growth process. Cobalt sulphate and Thiourea were used as the precursors [3]. Zhenrui Yu et al. deposited CoS thin films using a modified chemical bath deposition with cobalt dichloride and sodium sulfide aqueous solution as starting materials [4]. Semiconducting nanostructures are promising candidates for future electronic and photonic devices. They have unique physical and chemical properties and can be used as elementary units of optoelectronic devices [5].

This technique is novel in the sense that it possesses a number of advantages over conventional thin film deposition method. It is cheap, easily reproducible and can be used to coat large surface area of material. The technology is based on controlled release of metal ions (m^{+2}) and sulphide ions (S^{-2}) in aqueous solution of relevant compounds into which substrates are immersed [6]. The basic principle involved is that for a given compound to be precipitated from a solution its ionic product (IP) must exceed its solubility product (SP). When this condition is satisfied, the thin film of a particular compound is formed on the immersed substrate by an ion-by-ion condensation process [6, 7, 8, 9].

In the present experimental work CoS thin films were deposited on microscopic glass substrate using aqueous Ammonia and TEA as the complexing agent by Chemical bath deposition method. The structural properties were studied by X-ray diffraction technique and the optical characteristics were studied by using US-VIS-NIR Spectrophotometer UV-3600.

II. EXPERIMENTAL DETAILS.

Cobalt sulphide thin films were deposited by Chemical bath deposition method. The CBD method is most simple, inexpensive and convenient for large area deposition and inhibits good quality nanocrystalline thin films. The films so deposited are metal chalcogenide and metal oxide thin films which are technologically applicable in devices such as solar cells, photoconductive cells, photo electrochemical cells, dye sensitized cells, gas sensors, solar selective coatings, etc., where large surface area is required.

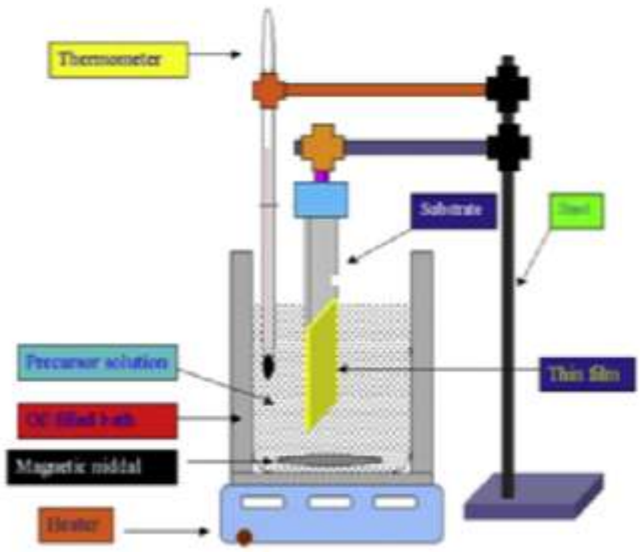

Fig.1. Thin Film Chemical bath deposition experimental setup.

The necessary apparatus like glass beakers, measuring cylinders, stirring rod, glass slides were first washed with detergent and rinsed with double distilled water and then dried in open air. The glass slides were used as substrates for the film deposition were first degreased by HCl for 24 hours and then washed with detergent solution and rinsed twice with double distilled water. Aqueous solutions of Cobalt sulphate and Thiourea of 1M concentration were first prepared using double distilled water. 2.8 ml TEA and 18 ml Ammonia were added drop by drop as complexing agents to the reaction mixture of 10 ml of Cobalt sulphate and 10 ml of Thiourea with constant stirring. The reaction mixture was diluted to 50 ml by adding double distilled water. The p^H of the reaction mixture was maintained between 10 to 10.5. The beaker with reaction mixture was kept in a paraffin oil bath whose temperature was maintained constant at about 326K. Then the slides were suspended by a slide holder and immersed in the beaker with reaction mixture for 90 minutes as shown in fig.1 above. Then the glass slides were removed, rinsed with double distilled water and dried in open air. The optical UV-VIS absorption measurement of the deposited thin film was done by using UV-VIS-NIR Spectrophotometer (double beam Shimadzu-3600) in the wavelength range of 320 nm to 1000 nm. X-ray powder diffraction analysis was done for structural characterization of the film using X-ray powder diffractometer.

The chemical reaction of the CoS thin film deposition is as depicted below:-

$$CoSo_4 + 4\,NR_3 \rightarrow Co\,(NH_3)_4^{++} + So_4^{--}$$
$$Co\,(NR_3)_4^{++} \rightarrow Co^{++} + 4NR_3$$
where R = H/ $CH_2\,CH_2OH$
$$(NH_2)_2CS\ 2OH \rightarrow HS^- \rightarrow CH_2N_2 + H_2O$$
$$HS^- + OH^- \rightarrow S^{--} + H_2O$$
$$Co^{++} + S^{--} \rightarrow CoS$$

III. Results and Discussion.

1. Structural Properties

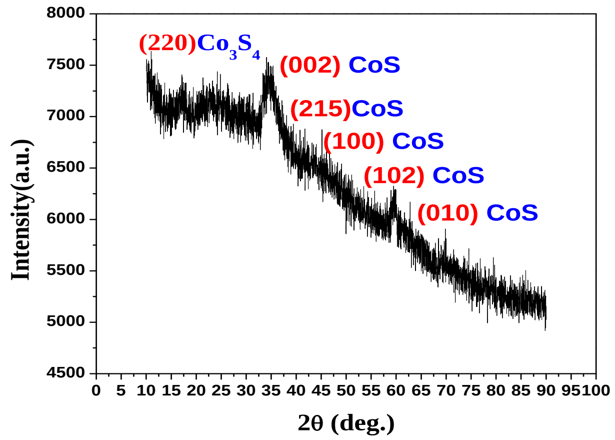

Fig.(2).X-ray diffractogram of CoS.

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Table.1.Structural parameters of CoS thin films deposited at optimised conditions of TEA concentration = 2.8ml, NH_3quantity = 18ml, Temperature = 326 K, p^H = 10.5

2θ Obs. Deg.	2θ Std. Deg.	d (^{0}A) obs.	d (^{0}A) std.	I/I_{ma} Obs.	I/I_{ma} Std.	Phase CoS	Phase Co_3S_4
26.4	26.586	3.373	3.35	96	20	------	220
34.42	34.674	2.603	2.585	100	4.5	2	-----
39.96	39.966	2.254	2.254	90	4	215	-----
41.98	41.989	2.15	2.15	89	9	100	-----
43.82	43.557	2.064	2.076	89	100	102	-----
59.68	59.555	1.548	1.551	84	2	10	-----

Figure.2. illustrates the XRD diffractogram of CoS thin film of thickness 660 nm deposited at substrate temperature of 326 K. The XRD pattern of as-deposited CoS thin film shows that the deposited CoS thin film is hexagonal in structure and polycrystalline in nature. Table.1. displays the XRD data of prominent peak formation at 2θ = 34.42^0 which corresponds to (002) planes with d value of 2.603 x 10^{-4} cm (PDF # 011279), at 2θ = 39.96^0 which corresponds to (215) planes with d value of 2.254 x 10^{-4} cm (Card No 00-001-1279), at 2θ = 41.98^0 which corresponds to (100) planes with d value of 2.150 x 10^{-4} cm (Card No 03-065-0407), at 2θ = 43.82^0 which corresponds to (102) planes with d value of 2.0640 x 10^{-4} cm (PDF # 190366), at 2θ = 59.68^0 which corresponds to (010) planes with d value of 1.548 x 10^{-4} cm (PDF # 047138). Another phase of Cobalt sulphide Co_3S_4 is observed at 2θ = 26.40^0 which corresponds to (220) planes with d value of 3.373 x10^{-4} cm (PDF # 190366).

The average crystallite size was calculated from (102) planes using Scherrer's relation as,

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

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 [10,11,12]. Nanocrystalline thin films are of significant interest for a large variety of electronic and optoelectronic devices [10,13,14]. The observed values of lattice parameters, intensities of reflections and d-values are in perfect agreement with the JCPD card No. 00-001-1279, 03-065-0407, PDF # 011279, PDF # 190366, PDF # 047138, PDF # 190366 respectively.

2. Optical Properties

A. Transmittance

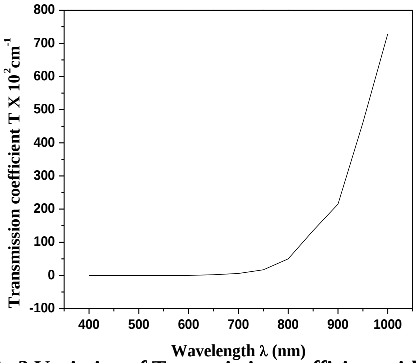

Fig.3.Variation of Transmission coefficient with wavelength for CoS thin films.

The optical transmission behaviour of Cobalt sulphide thin film was investigated in the wavelength range 380 – 1100 nm using US-VIS-NIR Spectrophotometer UV-3600. Fig. 3 shows a plot of Transmission coefficient (T) against Wavelength (λ) in nm. From Fig. 3 it is seen that the transmission coefficient T is lowest in the lower wavelength region and increases after 800 nm and linearly increases after 900 nm. This implies that the CoS thin film does not transmit the lower and visible wavelengths throughout the visible spectral region and transmits all the higher wavelengths in the Infra-red region of the spectrum. This further clarifies that the as-deposited CoS thin film is a very good absorber of lower and visible wavelengths of the solar spectrum.

B. Absorption Coefficient

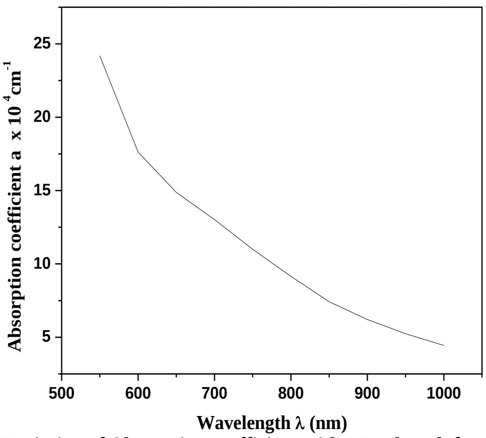

Fig.4. Variation of Absorption coefficient with Wavelength for CoS thin film.

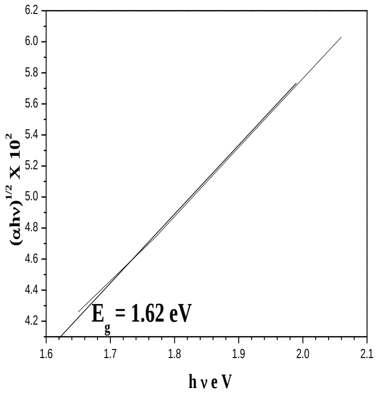

Fig. 6. Variation of Absorption Coefficient with Energy hν for CoS thin film.

Figure.4 illustrates the plot of variation of absorption coefficient α with the wavelength λ in the wavelength range 380 – 1100 nm. The absorption coefficient α is maximum of the order of $< 10^4$ in the UV and visible spectral region, which linearly decreases in the Infra-red region of the spectrum. This implies that the deposited CoS thin films are very good absorbers of lower and visible wavelengths. Hence the CoS thin film exhibits good optoelectronic property and can be used as potential materials in optoelectronic devices.

C. Optical Band gap Energy

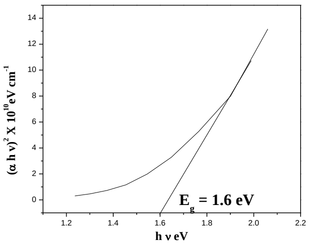

Fig.5.Variation of Absorption coefficient with Energy hν for CoS thin film

Figure. 5 shows a plot of $(\alpha h\nu)^2$ against (hν). The optical transitions are analysed from the classical relation ,

$$(\alpha h\nu) = \beta (h\nu - E_g)^n$$

Where β is a constant, depending upon the nature of semiconductor, E_g is the optical band gap energy and n is an index indicating the nature of optical transition during absorption process (n = ½ for direct allowed transition and n = 2 for an indirect allowed transition). The band gap energy was obtained from the intercept on Energy axis by extrapolation of the straight line graph of $(\alpha h\nu)^2$ against (hν) as shown in Fig.5. From Fig.5 the band gap energy was found to be E_g = 1.6 eV. In this case n = 1/2, so there is direct allowed transition. Figure.6 shows a plot of $(\alpha h\nu)^{1/2}$ against (hν). Here n = 2, hence there is indirect allowed transition. The band gap energy by indirect transition is found to be E_g = 1.62 eV. The nature of the above graphs shows that both direct and indirect transitions occur in the CoS film. The optical properties of the as-deposited CoS thin films show that they are direct band semiconductor and have mixed phases of CoS and Co_3S_4.

IV. CONCLUSIONS.

Cobalt sulphide thin films were deposited in the research laboratory by Chemical bath deposition method. The structural property of the deposited CoS thin film was studied by XRD measurements, which revealed that the films were polycrystalline with hexagonal crystal structure. The deposited CoS thin films were coffee brown in colour with 660 nm thickness. The average crystallite size was 47 nm. Hence the CoS thin films are nanocrystalline in structure. The optical properties of the CoS thin films revealed that the films had highest absorption coefficient α of the order of $< 10^4$ and lowest transmission coefficient T in the UV and visible region of the spectrum. The band gap Energy was found in two different sets E_g = 1.6eV by first transition i.e. direct energy transition and E_g = 1.62eV by second transition i.e. indirect energy transition. This confirms that there may be a mixture of two phases CoS and Co_3S_4 present in the film. These observed characteristics of the as-deposited CoS thin films state that they are very good potential materials for photovoltaic and optoelectronic applications.

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