Digest Journal of Nanomaterials and Biostructures Vol. 6, No 3, July – September 2011, p. 931 - 936

LIQUID PHASE CHEMICAL DEPOSITION OF COBALT SULPHIDE THIN FILMS: GROWTH AND PROPERTIES

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Synthesis of cobalt sulphide thin films (t≈ 537 nm) in an aqueous alkaline medium (pH = 11) on the glass micro slides using liquid phase chemical deposition process is presented. Cobalt sulphate and thiourea were used as the precursors. The deposition temperature and time were 56 ^{0}C and 80 minutes, respectively. The possible growth mechanism and reaction kinetics are suggested. Dark green coloured, tightly adhered, uniform, and diffusely reflecting deposits are obtained using this technique. An EDS analysis suggests that the deposits are Co-rich. The structural studies revealed hexagonal wurtzite structure of the CoS films with excellent match of the d-values and lattice parameters. The average crystallite size determined using FWHM method is in the nano range (≈ 15 nm). The absorption coefficient of the CoS thin film is high ($\alpha \approx 10^4 - 10^5$ cm^{-1}) and a direct band gap of 1.13 eV has been observed. The room temperature dc electrical conductivity is 5.25 x 10^{-6} (Ω cm)$^{-1}$ and activation energy of the intrinsic conduction is found to be 0.671 eV. The thermo probe measurements showed n-type conduction of the sample. Surface morphology shows a network of elongated thread like crystallites tapered at both ends, randomly oriented and threaded into each other.

(Received March 16, 2011; Accepted May 12, 2011)

Keywords: Liquid phase growth; Deposition parameter, Hexagonal wurtzite, Selective coating, IR-detector

1. Introduction

Metal chalcogenide thin films are assuming increasing interest in a variety of optical and optoelectronic devices viz. decorative coatings, solar absorbers, photo-detectors, and solar cells including recent photoelectrochemical solar cells [1-5]. Attempts were made to deposit a variety of metal chalcogenide thin films employing various deposition technologies individually [1,4,5,6-11] and very recently following a combinatorial approach for the development of new materials and device structures with new and improved properties offering a high degree of flexibility for substrate materials, deposition conditions and preparative parameters, and real time monitoring capability that helps to reduce sample size, time, and cost of the fabrication [12]. This requires development of new and complex deposition systems, the analysis, performance, and therefore development of new thin film materials is rather complex and tedious. Growth of the metal chalcogenide thin films via chemical solution deposition or chemical bath deposition or chemical growth process route has been one of the key technologies today [8-12] because it is the conventional method with the advantages of economy, convenience, easy scaling up to large area (even complex shapes) deposition, high degree of direct composition control and enabled recently oxide, nitride, and carbide films for optronic, hard coatings, and dielectric applications [8-12]. In view of the above advantages of the deposition process and diverse applications of the metal chalcogenide films, we have decided to initiate synthesis of cobalt sulphide thin films owing to

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*Corresponding author: laldeshmukh@gmail.com their possible usage in selective coatings and solar cells, optical filters, temperature sensors, optical wave guides and IR-detectors [1-3,13-16]; although they are scantily investigated.

A liquid phase chemical deposition process developed and modified by us and set for its deposition conditions and preparative parameters [4, 8, 9] was used for this purpose. The film growth process has been understood and few of the materials characteristics are explored in this paper.

2. Experimental details

2.1 Synthesis of the CoS samples

Cobalt sulphide thin films were synthesized from liquid phase of the reactants using our modified chemical deposition process [4, 8, 9, 17-19]. Cobalt sulphate and thiourea (both AR grade) were used as the pre-cursors. Initially, 10 ml (1M) solution of $CoSO_4$-$7H_2O$ prepared in double distilled water was taken in a glass beaker 250 ml in capacity. Appropriate quantities of triethanolamine and ammonia (25% AR, sp.gr.0.91) were added to form a complex and then 10 ml (1M) thiourea (A.R - grade) was added drop by drop with a continuous shaking (PH≈11). The total volume of the reaction bath was then made 150 ml with addition of double distilled water and the reaction container was transferred to a constant temperature (56^0C) oil bath. The glass slides (75 mm x 9 mm x 2 mm, chemo mechanically and ultrasonically cleaned) mounted on a specially designed substrate holder were attached to a constant speed motor and kept rotating with a 70 ± 2 rpm speed in the reaction mixture for 80 minutes. This helps for constant stirring / churning of the reaction bulk automatically that makes energetically favourable for continuous arrival of the Co^{2+} and S^{2-} species on the glass surface facilitating better orientation of the crystallites with improved grain structure [17-20]. The samples were taken off the reaction bath, washed with double distilled water, dried and kept in a dark desiccator.

2.2 Methods and measurements on the samples

The terminal layer thickness was measured by an interference technique. The film composition was determined using the EDS technique (KEVEX- 7000-77) with an accelerating voltage of 20 kV. The X- ray diffraction method was used to determine the structure of CoS films. An X- ray diffractometer, Philips – PW – 3710 (λ= 1.5406 A^0) was used for this purpose. The 2θ range used was from 20^0 - 80^0. The optical absorption studies were conducted on these samples in the range of wavelengths from 500 nm to 1300 nm and the band gap was estimated. The electrical conductivity was also measured in the 300K – to 550K temperature range and the type of conduction mechanism was determined. Surface morphology was viewed through a scanning electron microscope, CEMECA – SU – 30 [France]. The Au - Pd coating and accelerating voltage of 20kV were used for these studies.

3. Results and discussion

Cobalt sulphide is technically important class of semiconductor which has found direct applications in solar selective coatings, photo detectors, and solar cells and can be harnessed for possible usage in optical filters, thermal sensors, optical waveguides and as a DMS material by alloying/mixing with a suitable metallic phase. The chemical synthesis of cobalt sulphide thin films is only scantily studied [1, 5] under different deposition conditions and using different chelating agents and source materials. The deposition processes so far studied are pointed out to be complicated and cannot be controlled precisely [1, 10]. Additionally, almost all the deposition processes are time consuming and growth mechanisms and reaction kinetics suggested are different [1, 10]. In view of the above and being a vast experience of the solution growth process we have, for the first time, deposited cobalt sulphide thin films using our optimistic liquid phase modified chemical growth process [8, 9, 17-20].

In actual, synthesis of CoS thin films was carried out in a relatively high alkaline medium (PH≈11) on glass substrates which were previously degreased in concentrated nitric acid for 24 hours, washed with detergent solution and rinsed with double distilled water and dried ultrasonically. The degreasing of glass substrates provides nucleation / epitaxial centres on the surface of the glass that helps to initiate the film growth thereby yielding tightly adherent and highly uniform deposits. The growth solution consisted of 10 ml (1M) $CoSO_4$, 2ml TEA, 16 ml 25% ammonia, 10ml (1M) thiourea and 115 ml double distilled water, which were mixed in the above order. The Co^{2+} and S^{2-} ions react with each other and form neutral molecules either precipitates spontaneously or very slowly in highly alkaline medium. Fast precipitation means no film formation on the substrate surface; on the other hand, if the precipitation action is controlled and slow (with reaction additives like TEA or NH_3), then neutral molecules could get sufficient time and chance to initiate the formation of a thin solid deposit on the substrate surface, which is favoured energetically and enhanced by the reaction temperature and speed of the substrate rotation (in our case) [18, 19]. We propose the following reactions;

$$CoSO_4 + (TEA)_n \leftrightarrow [Co\,(TEA)]_n^{++} + SO_4^{--} \tag{1}$$

$$[Co\,(TEA)]_n^{++} \leftrightarrow Co^{++} + (TEA)_n \tag{2}$$

$$(NH_2)_2CS + 2HO^- \leftrightarrow S^{--} + 2H_2O + CH_2N_2 \tag{3}$$

$$Co^{++} + S^{--} \rightarrow CoS. \tag{4}$$

The deposits are thin, uniform, tightly adhered with substrate support, and diffusely reflecting with colour changing from light green (small thickness) to dark green (terminal layer thickness) during deposition. The terminal layer thickness was measured by an interference technique and found to be of the order of 537 nm for a double layered CoS. The as-deposited film was analysed for its composition by the EDS technique. Three spot locations were selected and average composition was determined. The deposits, at our experimental conditions, are Co-rich (Co≈80% and S≈20 %). The crystal structure was then determined using a Philips – 3710 X-ray diffractometer with CuKα line ($\lambda = 1.5406\ A^0$). The deposits are hexagonal polycrystalline and the diffractogram is shown in figure 1. The d-values, intensities of reflections, and lattice parameters have good match with JCPD data [5, 21].This is shown in table 1. The average crystallite size was determined using FWHM method and found to be in the nano range (≈ 15 nm). The optical absorbance of a good quality sample was then measured in the 500 nm to 1300 nm wavelength range. The absorption coefficient (α) is high (10^4-$10^5\ cm^{-1}$) and it has a broad absorption edge as expected for thin films. The optical band gap (E_g) was computed from the variation of $(\alpha h\nu)^2$ versus hν as shown in fig.2. CoS has a direct band gap of 1.13eV. The electrical conductivity and thermoelectric probe measurements were carried out in the 300K – 550K temperature range. At room temperature (300K), electrical conductivity is of the order of $5.25 \times 10^{-6}\ (\Omega\ cm)^{-1}$ and the activation energy of an intrinsic conduction is found to be 0.671 eV. The thermo probe measurements revealed n-type conduction and is in contradiction to the observations of Basu and Pramanik [5]. We attribute the observed conduction to the lack of stoichiometry in CoS in our case as revealed by an EDS analysis. The surface topography was viewed through a scanning electron microscope and a typical surface micrograph is shown in fig- 4. It appears that, at our experimental conditions, the film growth is like a network of long elongated crystallites tapered at both ends, randomly oriented, and threaded into each other.

Table 1. X-ray diffraction data of a typical CoS film prepared by LPCBD.

d(obs.) A^0	**d(std.) A^0**	**I/I_{max} (obs.)**	**I/I_{max} (std.)**	**CoS(H) planes**
2.915	2.918	100	62	100
2.563	2.538	93	45	101
1.927	1.929	76	100	102
1.687	1.685	70.7	43	110
1.497	1.478	67	5.2	103
1.447	1.459	69	4.4	200
1.405	1.412	63	10	112
1.289	1.285	59	4.2	004
1.251	1.268	60	16	202
	a=3.37 A^0	(std.)	a=3.336 A^0	(obs.)
	c= 5.14 A^0	(std.)	c= 5.156 A^0	(obs.)

H: hexagonal; d: interplanar distance; I/I_{max}: relative intensity.

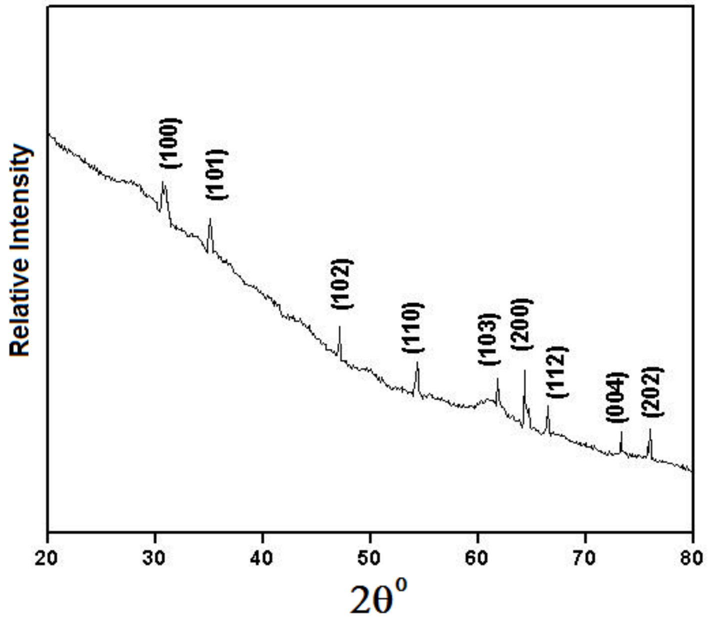

Fig. 1 XRD pattern for a typical CoS thin film.

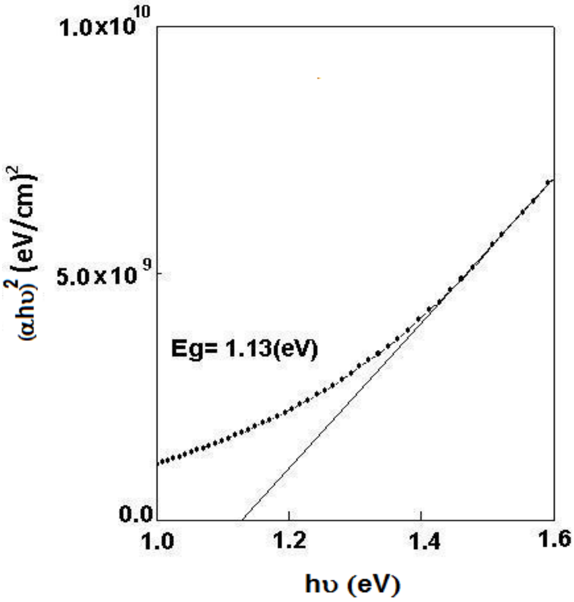

Fig. 2 Variation of $(\alpha h\upsilon)^2$ *vs.* $h\upsilon$ *for CoS thin film.*

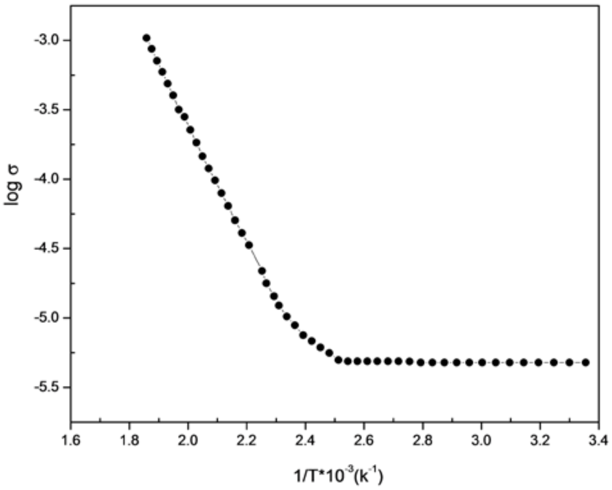

Fig. 3 Variation of log σ *with 1/T for CoS thin film.*

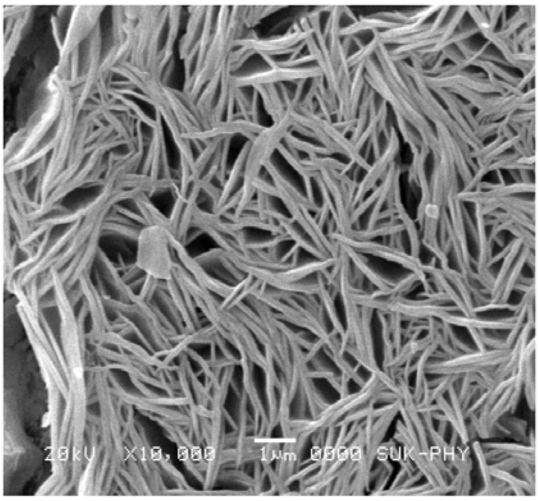

Fig. 4 SEM micrograph of a typical CoS thin film.

4. Conclusions

i) Growth of cobalt sulphide thin films is made possible from an aqueous alkaline medium.
ii) Dark green coloured, thin ($t \approx 500$nm) , tightly adherent, uniform and diffusely reflecting deposits are obtained at our experimental conditions (deposition temp. = 56^{0}C, time=80 mins, PH= 11±0.1).
iii) As- deposited CoS is crystalline Co rich with hexagonal wurtzite lattice and average crystallite size is in the nano range (≈ 15nm).
iv) Optical absorption of these samples is high (α=10^4-10^5 cm^{-1}) and the energy band gap is 1.13eV direct.
v) CoS exhibits semiconducting nature with an intrinsic activation energy of electronic conduction equal to 0.671 eV.
vi) At our experimental conditions CoS is n-type.
vii) Surface morphology shows a network of long elongated crystallites, randomly oriented and threaded into each other.

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