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Optical Characterization of Spray Deposited CoS Thin Films

M A Sattar, M Mozibur Rahman, M K R Khan, M G M Choudhury

***Abstract-** Cobalt sulfide thin films have been prepared by spray pyrolysis method on a glass substrate at constant substrate temperature 300°C.Structural, electrical and optical properties have been investigated. From XRD spectrogram, it is clear that the films are crystalline in nature with hexagonal structure having lattice constants, a=b=3.314 Å and c=4.604 Å. Scanning electron microscope (SEM) shows that Cobalt sulfide film exhibited more or less uniform and smooth surface morphology. The optical transmission spectra of the films show a two step transitions. For first step, energy gap varies from 1.35 eV to 1.4 eV and for second step 1.96 eV to 2.11 eV, respectively. The value of the absorption coefficient is >104 cm-1.For cobalt sulfide thin films of different thickness (118 nm and 195 nm) the direct band gap energy varies from 1.35 to 1.4 eV for first step of transition and from 1.96 to 2.11 for second step of transition. The indirect band gap energy varies from 1.25 to 1.3 for first step and from 1.78 to 1.89 for second step of transition. From the nature of graph it may be predicted that our deposited cobalt sulfide thin films are direct band gap semiconductor.*

***Keywords:** Spray pyrolysis; CoS; XRD; SEM, Optical Properties and Optical Band gap*

I. INTRODUCTION

Thin films are of current interest owing to their potential use in light emitting diodes and laser diodes. Besides this other photo-electronic device e.g., photovoltaic solar cells, photoconductive devices etc. are now under active consideration of the experimental physicists. Due to immense application of CoS thin film in optical and optoelectronic devices, such as solar energy absorber, solar cells and photo detectors [1-3], we have taken this material for study and planned to prepare cobalt sulfide thin films by spray pyrolysis method and to study in details on the structural and optical properties and to compare the results with those obtained by others. Recently, Cobalt sulfide thin films have been deposited using various techniques, such as vacuum evaporation [4-5], electro deposition [6], chemical bath deposition [7], modified chemical bath deposition etc. Among these techniques, for wide area deposition, spray pyrolysis [8] is one of the suitable techniques for CoS thin films deposition with low cost.

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II. EXPERIMENTAL DETAILS

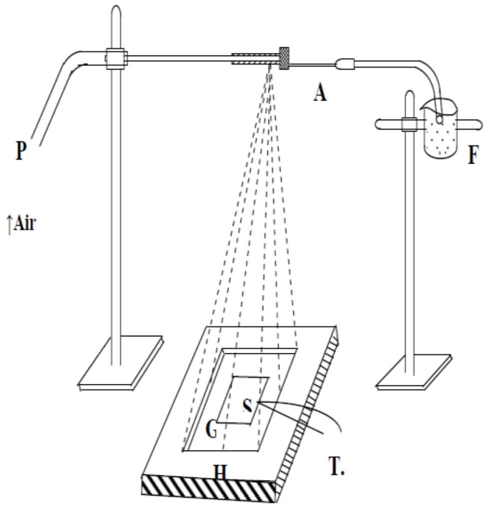
The working solution was prepared by taking 0.1M Cobalt chloride (LOBA Chemie, 97%) and 0.1 M sodium sulfide as source materials. The most commonly used solvents are water. As $CoCl_2$ and Na_2S dissolve in water at room temperature, sufficient amount of thiourea (LOBA Chemie, 99%) was added as an additional sulfur supplier.

Since the spray system used in the present experiments operates via a partial vacuum path at mouth of spray nozzle. The concentration of the solution prepared by the solvent should be such that it could at least drawn by the nozzle. The Probable chemical reaction that takes place during this process is given below:

$$CoCl_2.5\,H_2O + Na_2S + CH_4N_2S \xrightarrow[\text{Decomposes}]{300\,^{\circ}C} CoS + 2\,NaCl\uparrow + NO\uparrow + CO_2\uparrow + \text{Steam}\uparrow$$

The structural characterization of the films was performed using X-ray diffraction analysis. The XRD patterns of the films were taken with a diffractometer, X'Pert PRO XRD PW 3040, using Cu-Kα (λ = 1.54 Å) radiation with 60 kV-55 mA.

Optical transmittance and reflectance spectra were taken by using a double beam spectrophotometer. Measurements were made by placing the sample in incident beam and another empty substrate in the reference beam of the instrument. The optical transmission and reflection of the film with respect to glass substrate were taken for wavelength range 350 to 1100 nm using uv-1601 pc SHIMADZU VISIBLE SPECTOPHOTOMETER.



A - Lower tube, G - Steel plate, H - Heater S = Substrate, P = Compressed air (Upper tube) T. C. = thermocouple F = chemical solution (Beaker)

Fig. 1. Experimental set up of spray pyrolysis method for the preparation of CoS thin films.

III. RESULTS AND DISCUSSIONS

Cobalt sulfide thin films were prepared by spray pyrolysis method on glass substrate at temperature, T =300°C. All the measurements were done after annealing the films at 350°C for 1 hour in closed furnace.

A. Structural Properties

From XRD spectrogram in Fig.2, it is clear that the films are poor crystalline in nature. The XRD patterns could be indexed with hexagonal structure [JCPDS-02-1458]. The lattice constants were calculated and found to be, a=b=3.314 Å and c=4.604 Å. Crystallite size was calculated using the relation,

$\xi = 0.94\lambda/B\cos\theta$…………...…………...……. (1)

Where, ξ is the crystallite size, λ is the wavelength of the X-ray used, θ is the diffraction angle and *B* is the full width at half maximum (FWHM). The diffraction peaks at 2θ values have been chosen for calculation of crystallite sizes for CoS and Co_4S_3 [9-11] [JCPDS-042-0826].

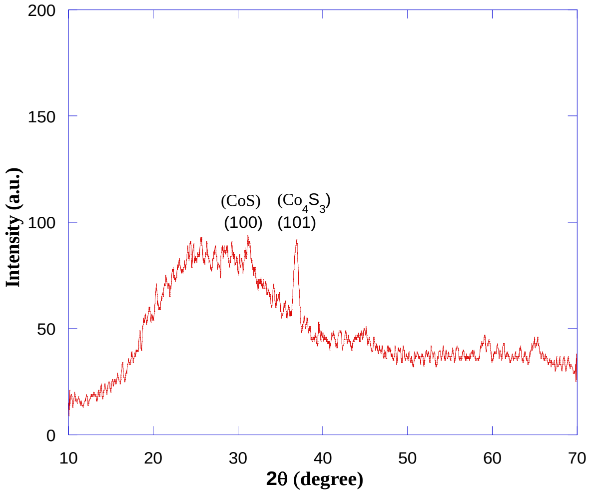


Fig.2. XRD patterns of cobalt sulfide thin films

B. SEM study of Cobalt Sulfide thin films

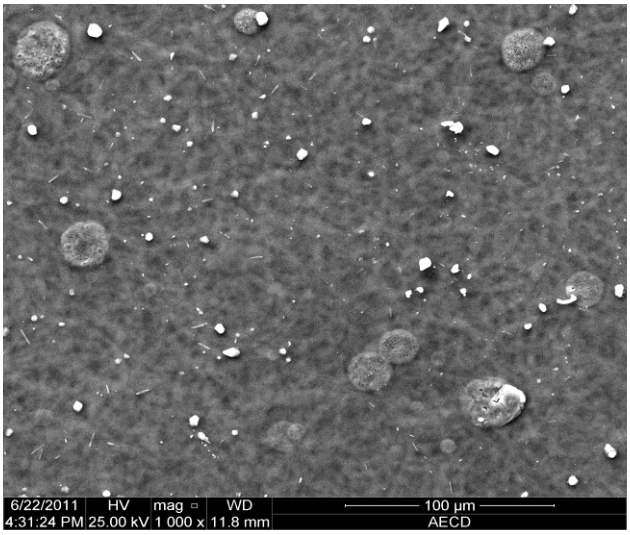


Fig.3. (a) 1000 magnification

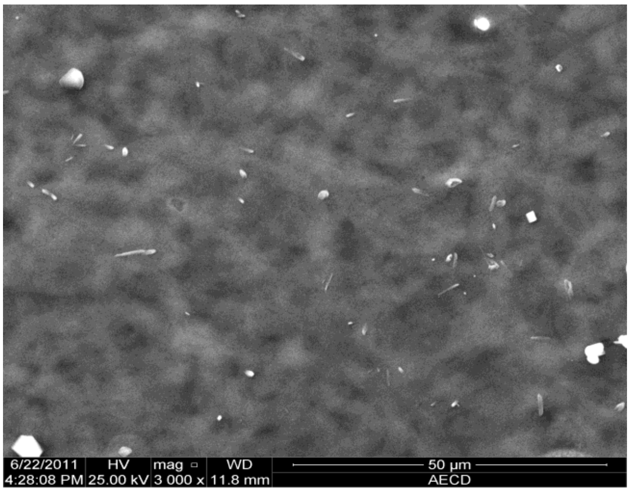


Fig.3. (b) 3000 magnification

Fig.3 (a), 3(b) SEM micrographs of as –deposited cobalt sulfide films with different magnification for 300°C temperature.

Surface morphology of the as-deposited, cobalt sulfide films on glass substrate were studied by scanning electron microscopy (SEM) under 1000, and 3000 magnification. Moreover uses of additional layer sometimes damage the film surface and distorted image is obtained. Fig.3 (a), 3(b), 4(a),.4(b) shows the SEM image of as-deposited cobalt sulfide film surface at 1000, and 3000 times magnification respectively at different temperature. SEM micrograph shows smooth surface. SEM shows of cobalt sulfide film exhibited more or less uniform surface morphology.

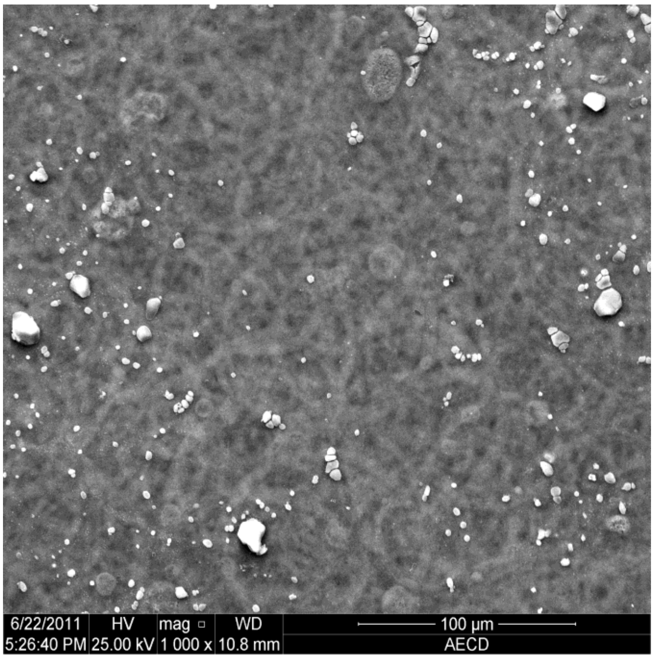


Fig.4 (a) 1000 magnification

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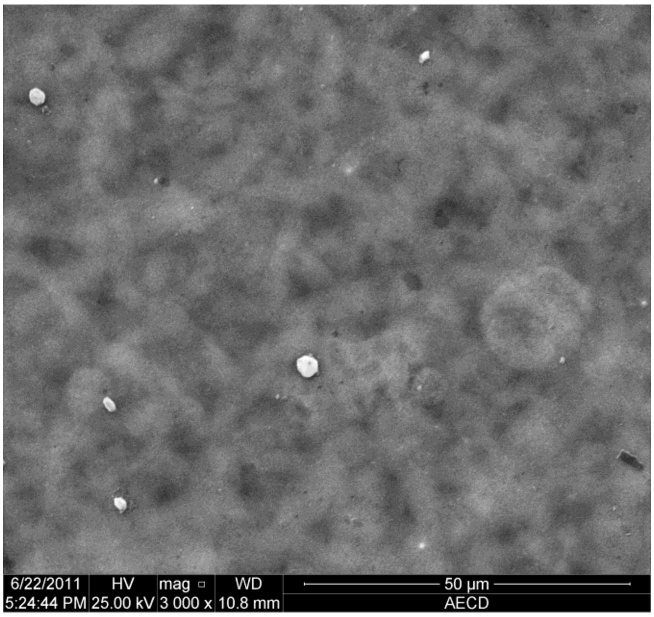

Fig.4 (b) 3000 magnification

Fig. 4(a), 4 (b) SEM micrographs of as-deposited cobalt sulfide films with different magnifications for 320°C temperature

IV. OPTICAL PROPERTIES

A Reflectance and Transmittance

The optical transmission and reflection spectra of cobalt sulfide thin films of different thickness were taken within the wavelength range 380 -1100 nm. The variation of obtained reflectance, R and transmittance; T of cobalt sulfide films having different thickness are shown in Fig. 5 and Fig. 6 respectively. Fig. 5 shows that reflectance first increase with the increase in wavelength the value reaches to a maximum and then slowly decreases, and again increases quite sharply and reaches to maximum value after which it become more or less flat. But transmittance first increases slowly in the lowest wavelength region and increases relatively sharply with wavelength near the absorption edge (Fig 6). It can be seen that each film has two steps transition.

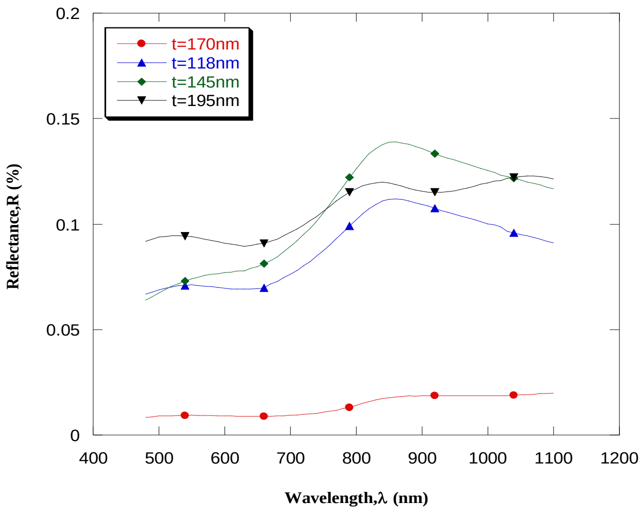

Fig.5. Variation of reflectance with wavelength for CoSthin films.

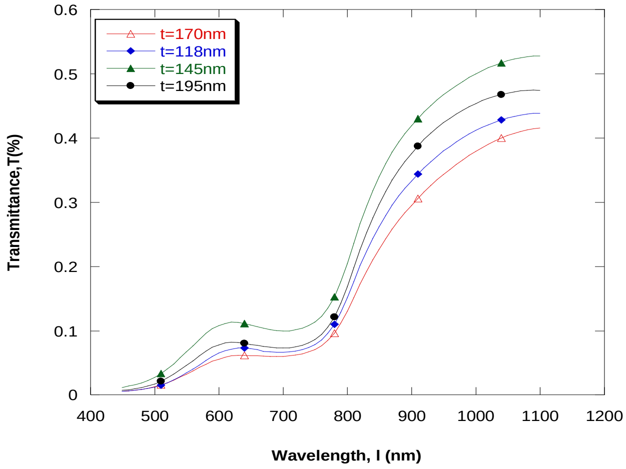

Fig.6. Variation of transmittance with wavelength for CoS thin films.

B. Absorption Coefficient

The absorption coefficient (α) for cobalt sulfide films was calculated from the transmission and reflection spectra using the relation $\alpha = \frac{1}{t} \ln\left[\frac{(1-R)^2}{T}\right]$, where t is the thickness of the film. Variation of α with photon energy of cobalt sulfide films having different thickness is shown in Fig. 7. From this figure, it is seen that the absorption coefficient first increases slowly in the low energy region i.e., at the higher wavelength region and then increases sharply near the absorption edge. Finally value tends to become saturated at higher energy (i.e. above 2.6eV). The absorption coefficient α depends on thickness of the film and increases as the film thickness increases. The absorption edge slightly shifts towards the higher energy with increasing films thickness. For higher photon energies the value of the absorption coefficient is $>10^4$ cm^{-1}.

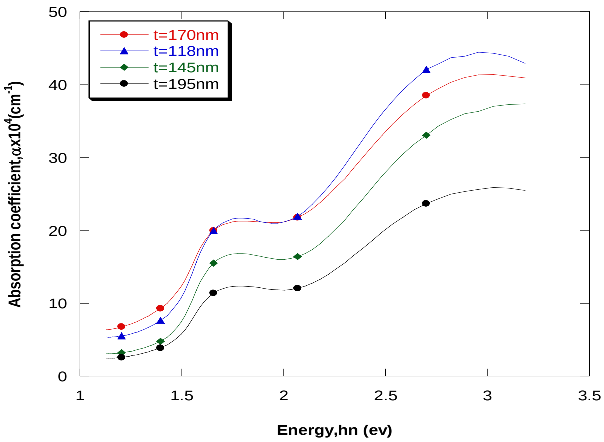

Fig.7. Variation of Absorption coefficient with energy for CoS thin films.

C. Optical Band gap

The optical transition are analyzed using the classical relation near absorption edge (for $\alpha > 10^4$ cm^{-1}).

$$(\alpha h\nu) = B(h\nu - E_x)^n$$

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Where β is a constant, depending the nature of semiconductor, E_g is the optical band gap, and n is an index related nature of the material and which is determined by the nature of the optical transition involved in the absorption process. (n = ½ for direct allowed transition and n = 2 for an indirect allowed transition). For the determination of band gap we have considered the direct and indirect allowed transition (n=1/2 and n=2 respectively). A plot of $(\alpha h\nu)^2$ vs. hν (direct allowed transition) of cobalt sulfide films having different thickness is are shown in Fig. 4. The band gap energy for each step of transition were obtained from the intercept of the energy axis after extrapolation of the straight lines section of $(\alpha h\nu)^2$ vs. hν curve. Fig. 5 shows the plot of $(\alpha h\nu)^{1/2}$ vs. hν (indirect allowed transition) of cobalt sulfide films of different thickness. Optical band gaps obtained for direct and indirect transitions are given in the Table 1. For cobalt sulfide thin films of different thickness (118 nm and 195 nm) the direct band gap energy varies from 1.35 to 1.4 eV for first step of transition and from 1.96 to 2.11 for second step of transition. The indirect band gap energy varies from 1.25 to 1.3 for first step and from 1.78 to 1.89 for second step of transition. From the nature of graph it may be predicted that our deposited cobalt sulfide thin films are direct band gap semiconductor. The direct and indirect band gap energy obtained is tabulated in Table 1. From the table it is seen that the obtained band gap energy for direct transition (first step) agree well with the reported value of cobalt sulfide thin films. [2].The band gap energy for calculated from second step of transition may be for Co_4S_3. From the optical measurement it is clear that the deposited films of cobalt sulfide are of mixed phases of CoS with Co_3S_4.

Table-1 Values of direct and indirect band gap energy for cobalt sulfide films of different thickness.

Film thickness t in nm	Direct band gap Energy E_g in eV		Indirect band gap Energy E_g in eV	
	1st Step transition	2nd Step transition	1st Step transition	2nd Step transition
118	1.35	1.96	1.25	1.78
145	1.37	2.00	1.27	1.84
170	1.38	2.06	1.29	1.85
195	1.4	2.11	1.3	1.89

From Table it is seen that the energy gap increases with increasing thickness for cobalt sulfide films. This result may be happened due to diminishing of defects or localized states with increasing film thickness of cobalt sulfide films.

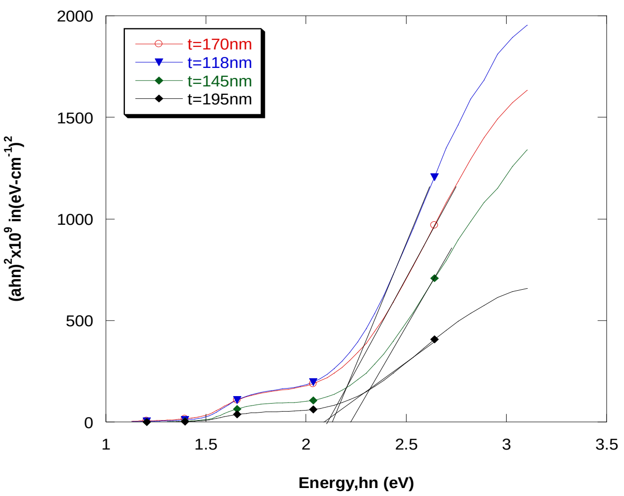

Fig.8. Variation of$(\alpha h\nu)^2$ with energy for CoS thin films.

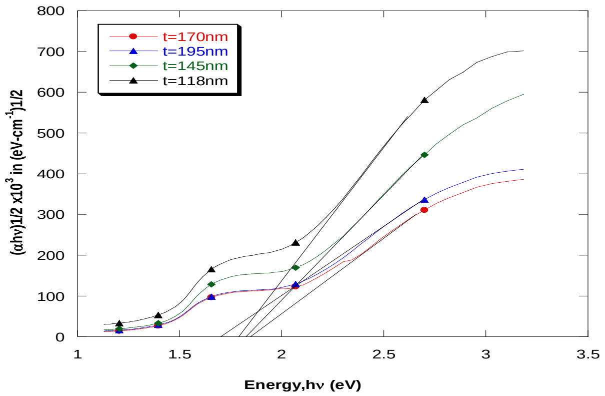

Fig.9. Variation of $(\alpha h\nu)^{1/2}$ with energy for CoS thin films.

V. CONCLUSIONS

Cobalt sulfide thin films were prepared by spray pyrolysis method. XRD measurements show that the films are crystalline in nature with hexagonal structure. SEM shows that Cobalt sulfide films exhibited uniform and smooth surface morphology.

The reflectance of cobalt sulfide thin films are relatively high (6-15%) in the visible wavelength range. It is more or less absorbing material ($\alpha > 10^4$ cm^{-1}) and two-step, transitions occur in optical energy transmission. Cobalt sulfide thin films are direct band gap semiconductor. Two different sets of energy gap were observed one for first transition (E_g~1.35 - 1.4 eV), and other for second transition (E_g~1.96 - 2.16 eV), and hence may be two phases of cobalt sulfide, CoS+Co_4S_3 are presence in the films.

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