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Electrical 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. Hall measurements indicate n-type semiconducting nature with carrier concentration ~10^{15} cm^{-3}. The resistivity gradually decreases with increasing temperature which indicates the semiconducting nature of the material. The conductivity increases slowly with increasing the temperature and reaches maximum at the higher temperature. Activation energy is comparatively high ($\Delta E > KT$) and the values vary from 0.19 eV to 0.38 eV in the low temperature region and 0.42 eV to 0.54 eV in the high temperature region, respectively.

Keywords: Spray pyrolysis; CoS; XRD; SEM, Electrical properties and Activation energy

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 electrical 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 is one of the suitable techniques for CoS thin films deposition with low cost.

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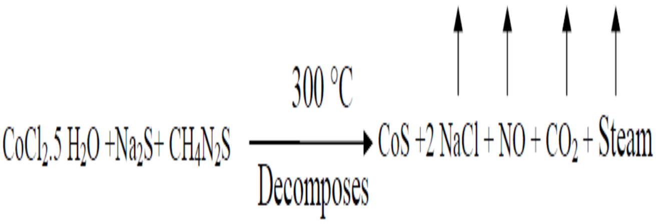
II. EXPERIMENTAL DETAILS

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 CoCl2 and Na2S 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:



The structural characterization of the films was performed using Xray 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. The Van Der Pauw's [8] specimen provided with four electrical contacts was used for the measurement of Hall Effect. Fine copper wires with silver paste made the electrical contacts. An electromagnet type provided the magnetic field used for the study of Hall effect. A designed and produced by Newport Instruments Ltd. England. In our work the gap between pole pieces was 2 cm. The current of the order of 8 amp was used for field 9.81 kGs. A voltage stabilizer was used so that a steady supply of current without fluctuation was maintained through the magnet. Van-der Pauw's method was used to measure the resistivity and electrical conductivity of the specimen. For electrical contacts were made at the four corners of the sample with indium dot point, where current is passed through any two terminal ,a electrometers was used to measure the current passing through two terminals and a digital voltmeter was used to measure the voltage developed between another two terminals. The resistivity (ρ) of thin films has been measured from room temperature to about 445 K by Van der Pauw's method. Measurements were done in vacuum at a pressure of about 103 Torr.

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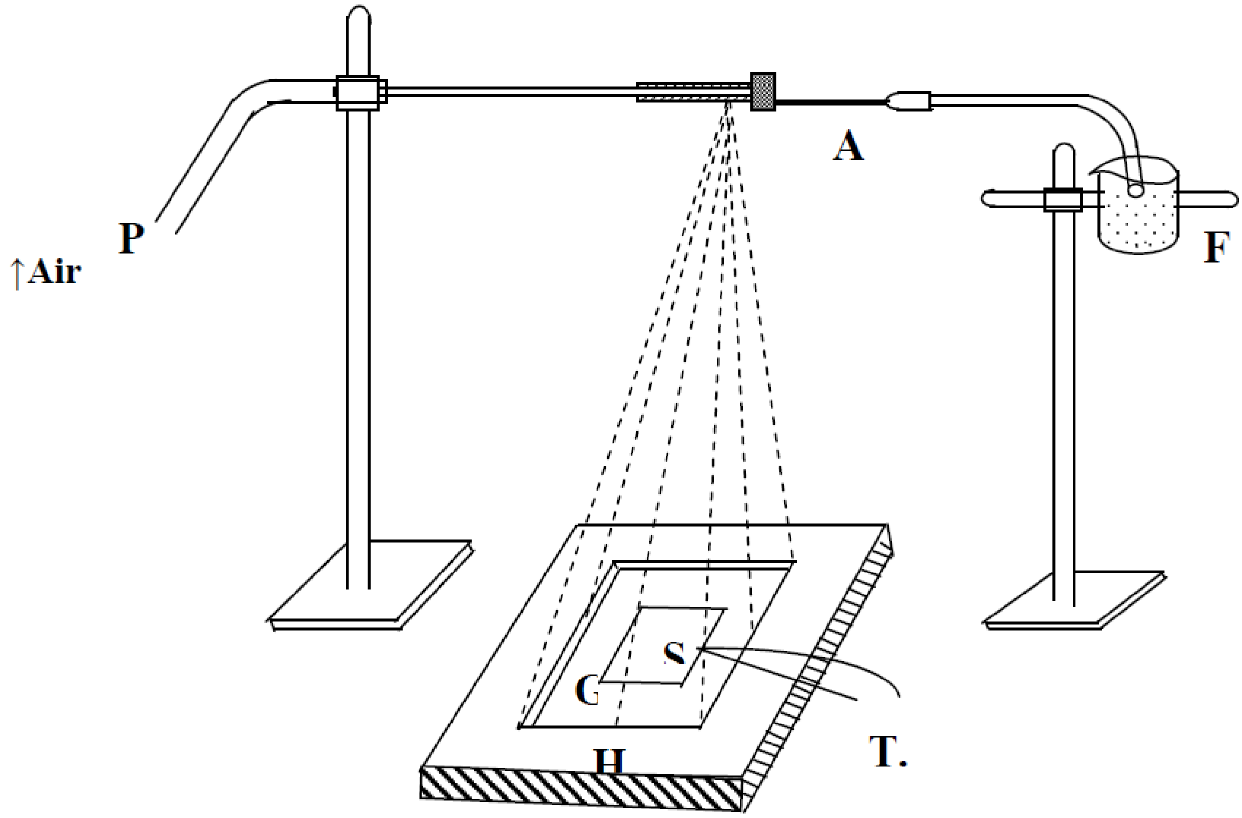

A - Lower tube, G - Steel plate, H - Heater S = Substrate, P = Compressed air (Upper tube) T. C. = thermocouple F = chemical solution (Beaker)

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.

3.1 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,

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

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]

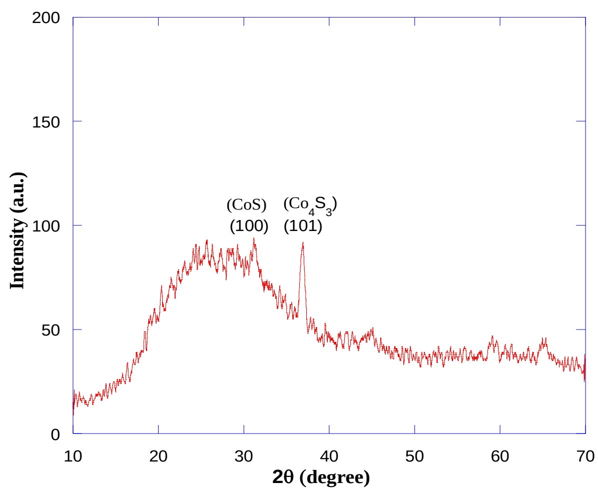

Fig. 2. XRD patterns of cobalt sulfide thin films

3.2. SEM study of Cobalt Sulfide thin films

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.

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SEM micrograph shows smooth surface. SEM shows of cobalt sulfide film exhibited more or less uniform surface morphology.

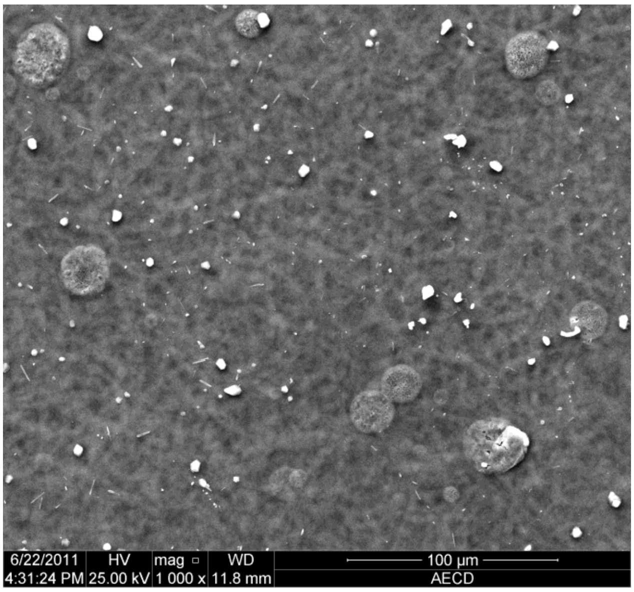

Fig. 3. (a) 1000 magnification

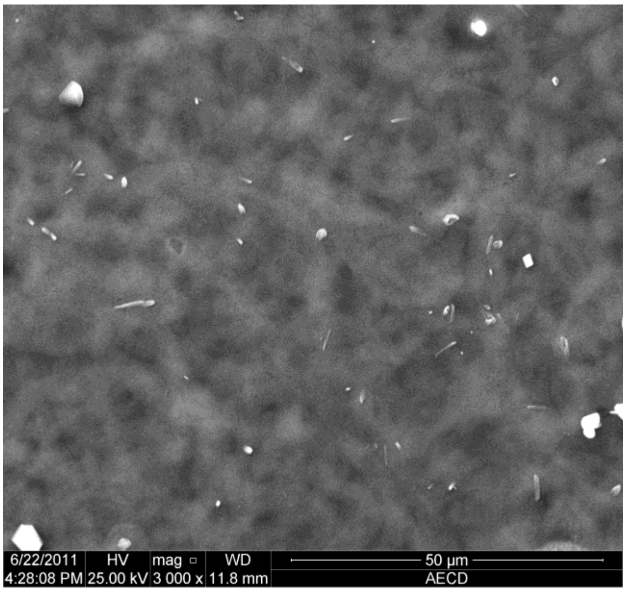

Fig. 3. (b) 3000 magnification

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

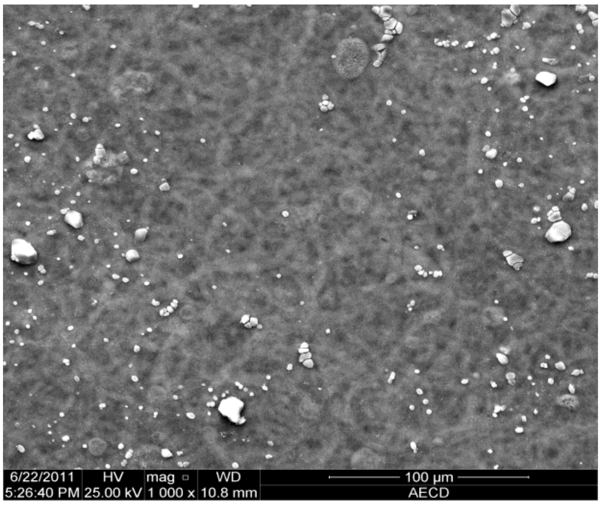

Fig. 4 (a) 1000 magnification

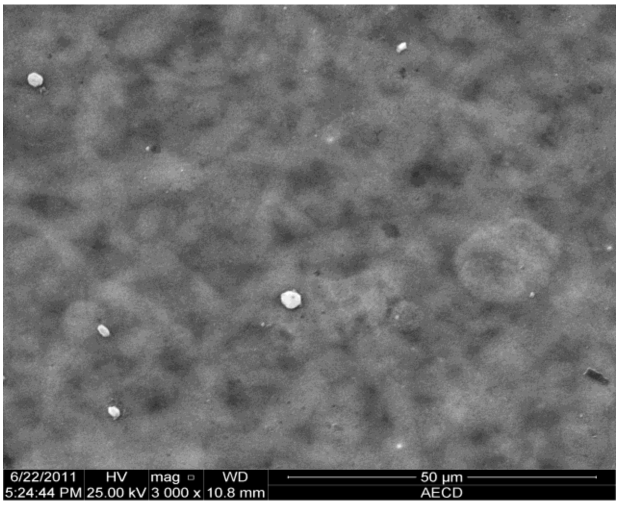

Fig. 4 (b) 3000 magnification

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

IV. ELECTRICAL PROPERTIES

4.1. Hall Coefficient, Hall Mobility and Carrier Concentration:

The variation of Hall constant (R_H), Hall mobility (μ_H) and carrier concentration (n) with increasing thickness of the films are shown in Fig 5,6 and 7. From Fig 5 it is seen that R_H decrease with increasing films thickness. But the mobility (μ_H) and carrier concentration (n) increase with increasing films Thickness (Fig.6 & 7). The measured values of R_H, $\mu_{H,}$ n and conductivity σ are tabulated in Table 1. The films are comparatively high resistive ($\rho \approx 10^2\ \Omega$-cm) moderate mobility (22 ~ 160 cm^2 /V-sec) and the carrier concentration is of the order of ~ 10^{15} cm^{-3}.

From the measurement of Hall effect it is seen that cobalt sulfide thin films have negative Hall coefficient (R_H) and this indicate the n-type behavior of cobalt sulfide thin films. The carrier concentration, n and Hall mobility μ_H increase with increasing films thickness may be due to diminishing the defects or localize states in the forbidden band with increasing thickness.

Table-1. Data for hall mobility, hall concentration and hall constant.

Film thickness in nm	Hall constant, R_H (cm^3/Coul)	Hall mobility, μ_H (cm^2 /V-sec)	Hall concentration, n × 10^{15} (cm^{-3})	Room Temp, conductivity × 10^{-2} (mho-cm^{-1})

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118	4500	26.1	1.33	0.58
145	3807	42.0	1.64	1.10
170	2827	70.5	2.21	2.5
195	2773	160.5	2.25	5.8

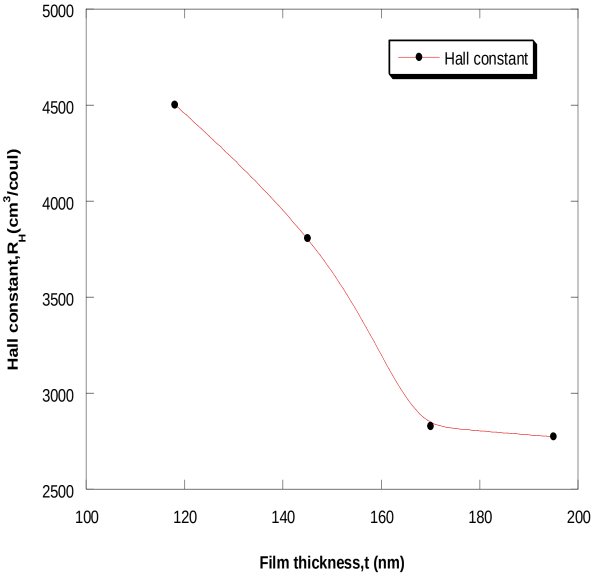

Fig.5. Variation of Hall constant(R_H) with thickness(t) for CoS thin films.

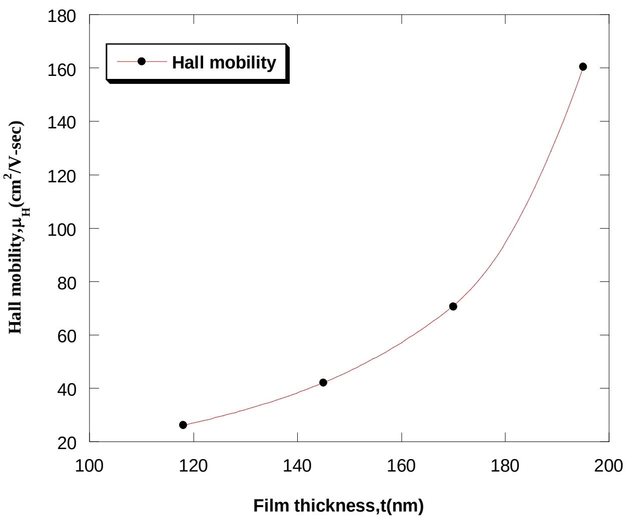

Fig.6. Variation of Hall mobility with film thickness for CoS thin films.

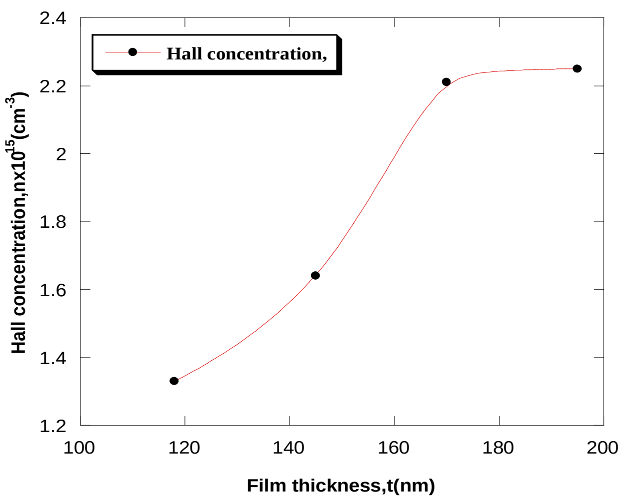

Fig.7. Variation of Hall concentration with thickness for CoS thin films

4.2. Variation of Resistivity with Temperature

Resistivity measurements were made by increasing the temperature quite slowly up to the maximum value 445 K. Films were then annealed at this maximum temperature i.e., at 445 K for half an hour. After annealing measurements were done by cooling the sample slowly to room temperature, the variation of resistivity with temperature for annealed films of a different thickness is given in Fig. 8. It is seen from this figure that resistivity gradually decreases with increasing temperature which indicates the semiconducting nature of the material. Fig. 9. Shows the variation of conductivity with temperature. The conductivity increases slowly with increasing the temperature and reaches maximum at the higher temperature. From this figure it is also seen that conductivity increases with increasing film thickness.

4.3. Activation Energy

Activation energy was calculated from the slop of σ vs. $\frac{1}{T}$ plot. Fig. 10 shows the plot of lnσ versus reciprocal of temperature for the films of different thickness of cobalt sulfide films. It is observed from the figure that in the high temperature region the plot has a greater slop and in the low temperature region the variation is almost linear with smaller slop. The activation energy ΔE was calculated from the relation. $\sigma = \sigma_o \exp\left(\frac{-\Delta E}{KT}\right)$. Where, k is the Boltzmann constant and σ_o is the pre-exponential factor. The activation energy ΔE_1 for low temperature region and ΔE_2 for high temperature region were calculated from the slope of the plots.

Table- 2. Variation of Activation energy with thickness.

Sample	Thickness (nm)	Activation energy, ΔE_2 (eV)	Activation energy, ΔE_1 (eV)
CoS	118	0.43	0.38
	145	0.46	0.26
	170	0.54	0.34
	195	0.42	0.19

The activation energy ΔE_2 is slightly higher than that of ΔE_1 but the values both ΔE_2 and ΔE_1 are comparatively high, which indicates free band transition (i.e. transition from localized state to conduction state) for both cases. At higher temperature the activation energy increases may be due to addition of little percentage of band-to-band transition carriers with free band transition carrier. This high activation energy nearly equal to the half of the band gap of cobalt sulfide thin films which is same as reported by Zhenrui Yu et al. [1]

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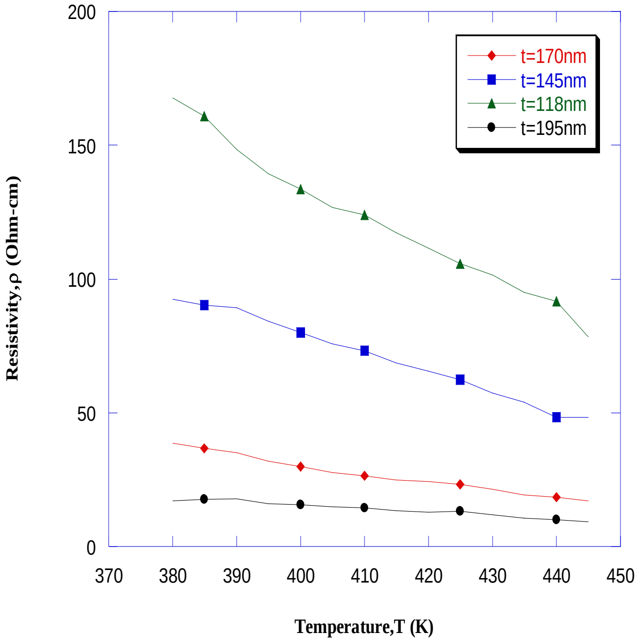

Fig.8. Variation of Resistivity with Temperature for CoS thin films.

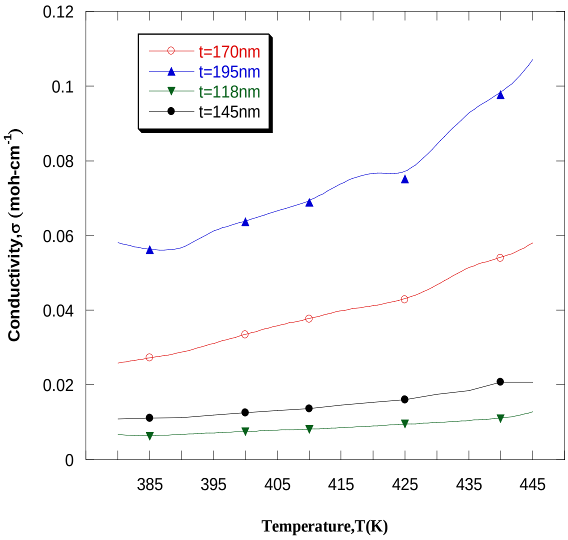

Fig.9. Variation of conductivity with temperature for CoS thin films

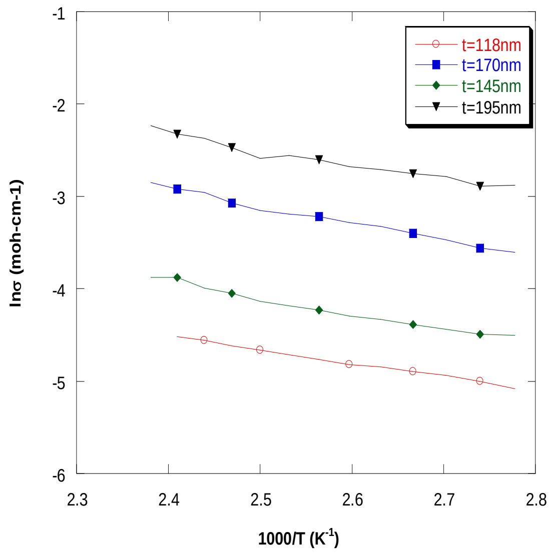

Fig.10. Variation of lnσ with (1/T) inverse temperature for CoS thin films.

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. It was found that prepared cobalt sulfide thin films are n-type material. Resistivity of cobalt sulfide thin films gradually decreases with increasing temperature which indicates the semiconducting nature of that material. It is a high resistive film ($\rho \sim 10^2$ Ω-cm). At higher temperature the activation energy increases may be due to addition of little percentage of band-to-band transition carriers with free band transition carrier.

VI. ACKNOWLEDGEMENT

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