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A STUDY OF THE THERMAL AND DIELECTRIC PROPERTIES OF COBALT SULFIDE THIN FILMS PREPARED BY SPRAY PYROLYSIS TECHNIQUE

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ABSTRACT

Cobalt sulfide thin films have been prepared by spray pyrolysis method on a glass substrate at constant substrate temperature 300°C. The films are characterized by thermal and dielectric properties. The thermoelectric power was calculated from the thermal e.m.f measurements. Experiment shows that negative thermoelectric power which indicates n-type behavior of the material. From thermoelectric power 'S', the scattering factor A, low temperature activation energy E_0, coefficient of activation energy, γ and scattering index, r have been calculated. The values of the E_0 vary from 0.01 to 0.11. The values of r lies between 0.5 to 1.5 and the values of A lies between 2.9 to 4.0 suggesting a mixed scattering mechanisms (ionized and impurity) are involved in the conduction process. Refractive index varies with thickness (1.3-2.6) but does not vary remarkably with photon energy. Real part of dielectric constant (1.3 - 8.0) depending on thickness also does not vary remarkably with photon energy.

Keywords: *Spray Pyrolysis, Dielectric constant, Refractive index, Activation energy.*

1. 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 (Ortega Borges *et al.,* 1994; Basu *et al.,* 1986), we have taken this material for study and planed to prepare cobalt sulfide thin films by spray pyrolysis method and to study in details on the thermal and dielectric 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, electro deposition, chemical bath deposition, 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.

2. 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:

$$CoCl_2.5\,H_2O + Na_2S + CH_4N_2S \xrightarrow{300°C} CoS + 2NaCl + CO_2 + NO + Steam$$

To measure thermoelectric power (TEP), one end of the specimen was held at ice temperature and the other end is heated to a temperature (K). Temperature of the sample was varied by varying voltage of a small heater from 298 K to 450 K. The copper-constantan thermocouple was used to measure the temperature of the sample. Digital multimeter measured the thermal emf generated by the specimen. The real part of refractive index was measured by computing and using optical transmittance and reflectance spectra. The real and imaginary parts of dielectric constant were calculated from the real part of refractive index. 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-6101 pc SHIMADZU visible spectrophotometer.

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3. RESULTS AND DISCUSSIONS

Two sets of cobalt sulfide thin films were prepared by spray pyrolysis method on glass substrate at temperature, 300 °C. One set for the characterization of electrical & optical properties and other set for the measurement of thermoelectric power. All the measurements were done after annealing the films at 350 °C for 1 hour in closed furnace.

3.1 Thermoelectric effect

For the measurement of thermoelectric power, +ve terminals of the voltmeter was connected with hot junction and –ve terminals with cold junction of the films. Copper-constantan thermocouple was used for the measurement of temperature. The variation of thermal e.m.f with temperature for cobalt sulfide thin films having different thickness is shown in Fig. 1. From the figure it is seen that, at room temperature the thermal e.m.f is positive which decreases with increasing temperature. The positive value of thermal e.m.f indicates that the semiconductor is n-type. At room temperature the prepared samples are n-type material but as the temperature increases the concentration of electrons decreases, this means they are compensated by holes. The thermoelectric power, S of the samples was determined from the thermal emf by using the relation $S = \pm \Delta V/\Delta T$. The variation of thermoelectric power, S with inverse of temperature, T for CoS thin films of different thickness is shown in Fig 2. The constant value of thermoelectric power in the low temperature region indicates the pinning of Fermi energy in the forbidden gap at this temperature. The temperature dependence of S is observed to follow the relation [N. F. Mott *et. al.* 1979], $S = \pm \frac{k_B}{e}\left(\frac{E_C - E_F}{k_B T} + A\right) = \pm \frac{k_B}{e}\left(\frac{E_0}{kT} - \frac{\gamma}{k} + A\right)$

Here $E_C - E_F = E_0 - \gamma T$ for a limited range of temperature, E_0 is the activation energy at very low temperature, γ is the temperature coefficient of activation energy and A is a constant related to the scattering index as $A = r + \frac{5}{2}$ for amorphous and polycrystalline semiconductor and whose value varies from 0 to 4. Here r is a scattering index depends on the type of scattering mechanism in the film. Fig. 3 shows the variation of Peltier coefficient, Π with temperature. The value of activation energy E_0 for limited range of temperature was calculated from the intercept of Π vs T plot (y-axis at T=0). The scattering factor A was determined from the intercept of S vs 1/T plot (y-axis at 1/T = 0). The temperature coefficient, of activation energy γ was determined from the slop of Π vs. T plot. The obtained values of E_0, A, γ and r for thin films of different thickness are tabulated in Table 1. It is observed that S, E_0 and γ vary with thickness Measured by Newton's ring methods. This non-systematic variation of TEP, S is probably due to secular surface scattering of the carries as mentioned (Damodara *et al.,* 1995). The value of scattering index, r is different for different thickness of the film, implies different scattering mechanism may involved in carrier transport. It may be predicted from the classical experience ($\mu \propto T\gamma$) the scattering factor $r = +\frac{3}{2}$ correspond to ionized impurity scattering and $r = +\frac{1}{2}$ is subject to grain boundary scattering (Khan *et al.,* 2003).

3.2 Refractive index

The refractive index is determined by computing the reflection data using the Hadley and Dennison relation (Hadley and Dennison, 1947). The variation of refractive index with photon energy for cobalt sulfide films of different thickness is shown in Fig. 4. Fig 4 shows that refractive index slightly increases with photon energy and also with the thickness of the films. For cobalt sulfide films the refractive index varies from 1.26 to 2.68 for the (1.13eV-1.42eV) energy range we have measured.

Table 1: data for E_0, A, γ and r

Sample	Thickness (nm)	A	$\gamma \times 10^{-4}$ ($eV\,K^{-1}$)	E_0 (eV)	$r = A + \frac{5}{2}$
CoS	85	4.0	5.09	0.047	$+\frac{3}{2}$
	135	2.9	6.90	0.01	$+\frac{1}{2}$
	170	3.7	6.38	0.041	+1.2
	198	3.8	6.03	0.11	+1.3

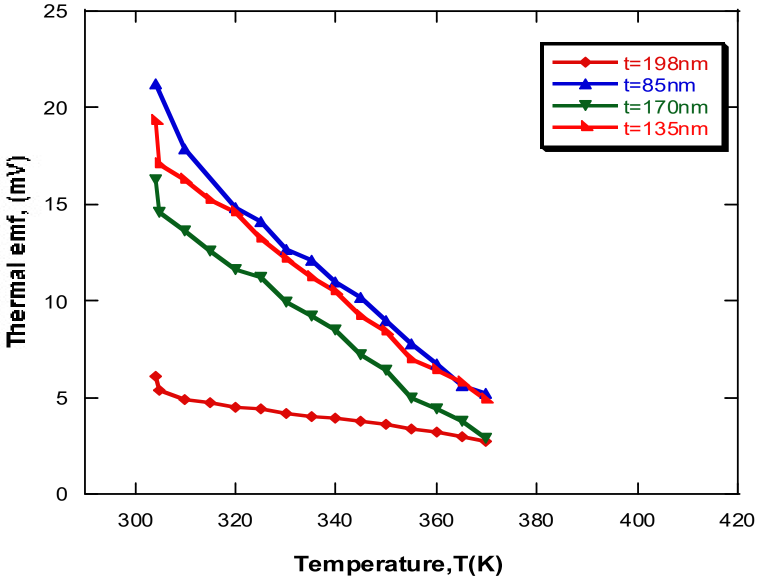

Fig.1 Variation of thermal emf with temperature for CoS thin films.

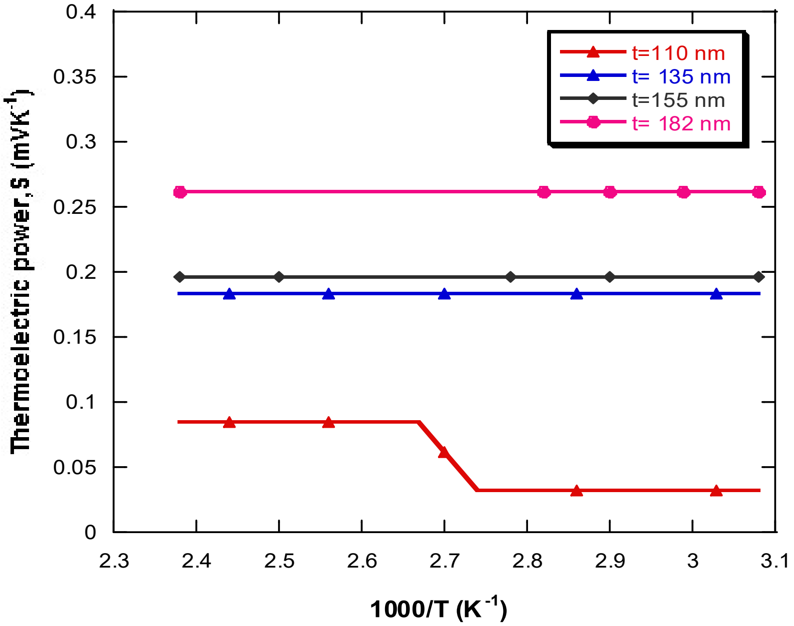

Fig.2 Variation of thermoelectric power with inverse temperature for CoS thin films.

3.3 Dielectric Constant & Dielectric Loss

The real and imaginary part of dielectric constant of cobalt sulfide films are determined by the following relations

$$\varepsilon_1 = n^2_0 - k^2_0$$

$$\varepsilon_2 = 2n_0k_0$$

And dielectric loss factor has also been calculated using the relation tan $\delta = \frac{\varepsilon_2}{\varepsilon_1}$ .The variation of real part of dielectric constant for cobalt sulfide films is shown in Fig. 5. Real part of dielectric constant ε_1 slightly varies with photon energy, but this value varies remarkably with thickness of the films. Figure shows that the variation of ε_1 is not systematic with films thickness. Value of ε_1 varies from 1.25 to 8.14 for cobalt sulfide with the photon energy. The variation of imaginary part of dielectric constant for cobalt sulfide films is shown in Fig. 6.The figure shows that in the lower energy region the value of ε_2 remains almost constant but increases at higher energy region. From this figure it is seen that the variation of ε_2 is not systematic with thickness. The variation of loss factor with energy for cobalt sulfide films is shown in fig. **7**. The variation of loss factor with energy is similar as imaginary part of ε_2.

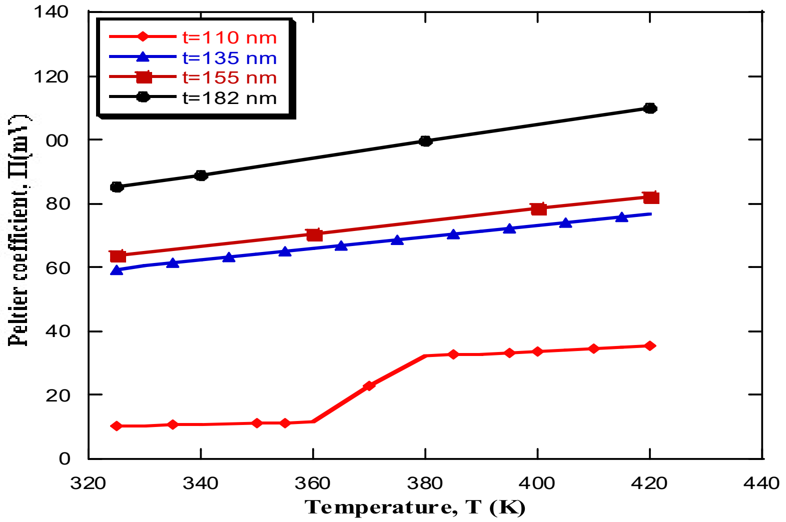

Fig 3. Variation of Peltier Coefficient with temperature for CoS thin fillms.

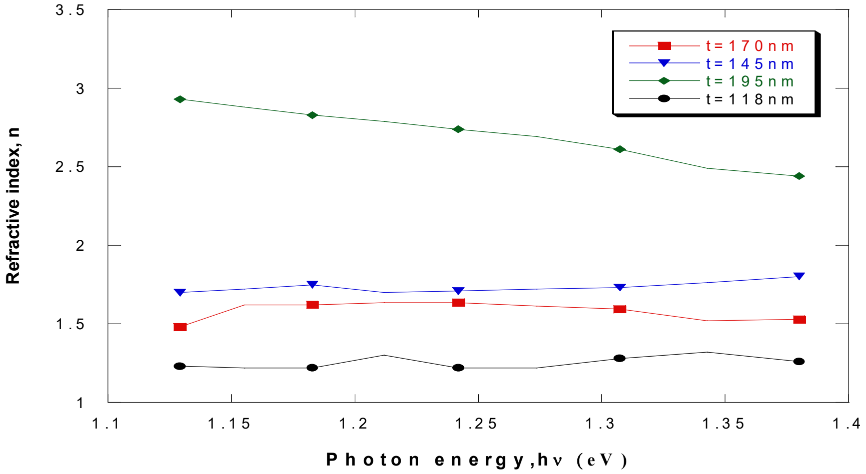

Fig.4 Variation of refractive index with photon energy for CoS thin films.

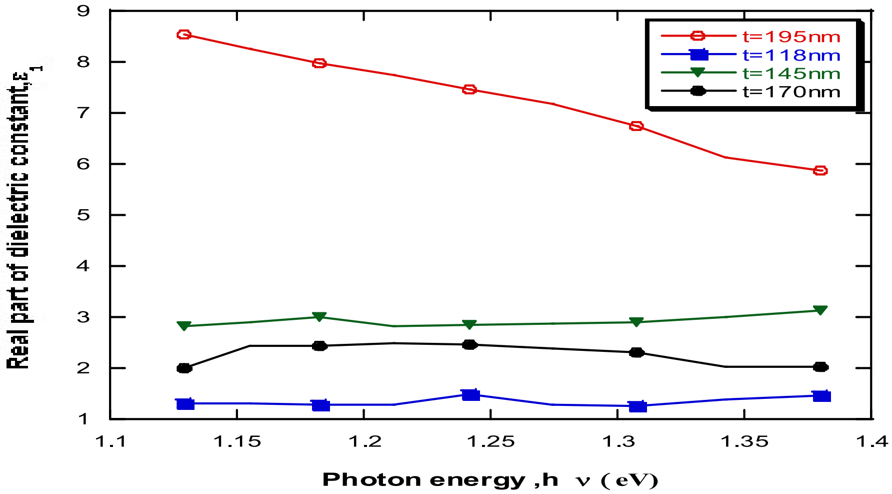

Fig .5 Variation of real part of dielectric constant with photon energy for CoS thin films.

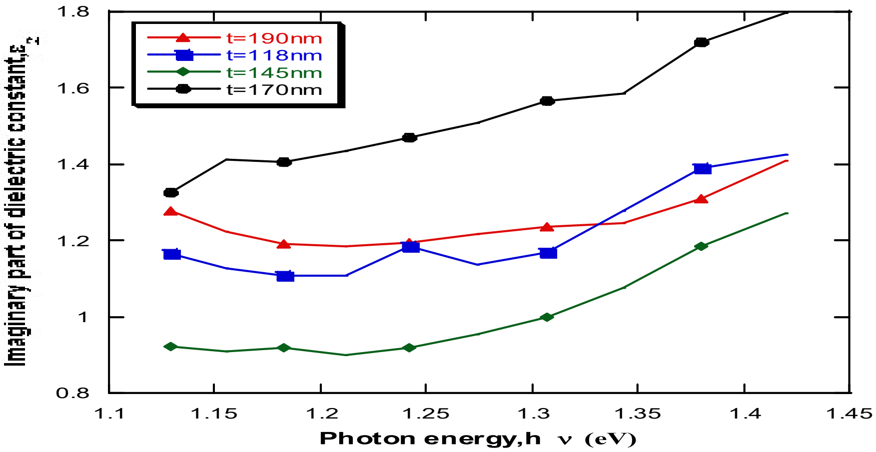

Fig.6 Variation of imaginary part of dielectric constant with photon energyfor CoS thin films.

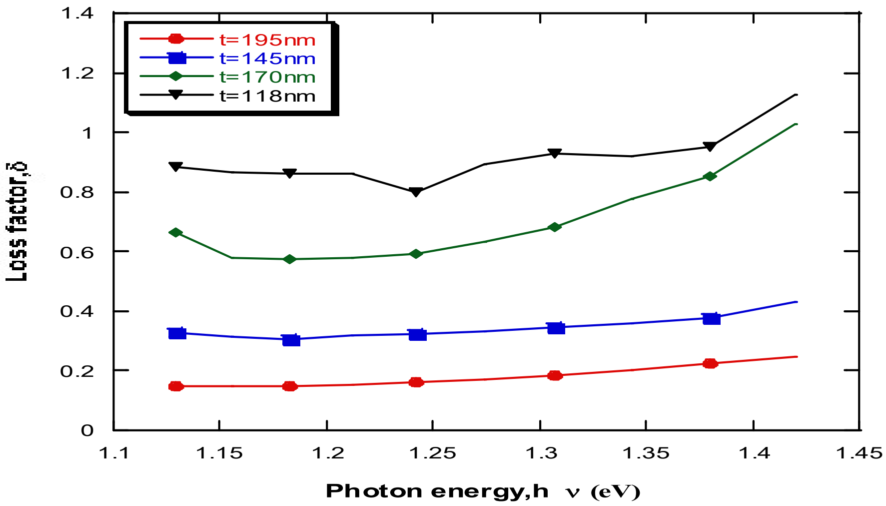

Fig.7 Variation of loss factor with photon energy for CoS thin films.

4. CONCLUSIONS

In the present work, cobalt sulfide thin films were prepared by spray pyrolysis method. Films of different thickness deposited on glass substrate at constant substrate temperature 300 °C. Different Physical properties such as thermo electric and dielectric properties have been studied. Prepared cobalt sulfide thin films are n-type material. In conduction mechanism free band transition are observed and the obtained activation energy is found to be relatively high value ($\Delta E_g \sim 0.42 - 0.56$ eV). The cobalt sulfide films have negative thermoelectric power. Scattering factor A, is relatively high, (2.9 - 4.0) and ionized scattering predominant in the scattering mechanism. It is more or less absorbing material ($\alpha > 10^4$ cm^{-1}) .Refractive index varies with thickness (1.3 - 2.6) but does not vary remarkably with photon energy. Real part of dielectric constant (1.3 - 8.0) depending on thickness also does not vary remarkably with photon energy.

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REFERENCE

Basu P. K., P. Pramanik; Mater, Sci. Lett.5 (1986)1216

Damodara Das V and Balmlayan C ; Jpn J Appi phys ,34 534 (1995)

Hadley, L. N. and Dennison, D. M.; (1947) J. opi.soc Am 37. 451

Khan M. K. R., M. Mozibur Rahman, Y. Zaman, M. G. M. Choudhury and M. O. Hakim; Vol.31 (2003), ISSN 1681-07

Mott N. F and Davis E A.; Electronic process in noncrystalline materials, Clarendon press, Oxford (1979)

Ortega Borges R., D. Lincot J.; Electrochem.Sol.140 (1994) 3464