International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Online International Journal Available at http://www.cibtech.org/jpms.htm
2013 Vol. 3 (4) October-December, pp.73-77/Ibrahim and Ubale

Research Article

CHARACTERIZATIONS OF NANOCRYSTALLINE SPRAY DEPOSITED CdS: FeS THIN FILMS

Ibrahim S.G. and *Ubale A.U.
Nanostructured Thin Film Materials Laboratory, Department of Physics, Govt. Vidarbha Institute of Science and Humanities, VMV Road, Amravati 444604, Maharashtra, India
**Author for Correspondence*

ABSTRACT
Synthesis of nanostructured composite chalcogenide materials has been the subject of much interest in basic research because of their novel physical and chemical properties. The ternary composite semiconducting thin films of CdS: FeS were successfully deposited onto glass substrates from aqueous solutions of ferric chloride, cadmium chloride and thiourea using at 573K temperature by using spray pyrolysis method. The films were characterized by using X-ray diffractometer (XRD), two point dc electrical resistivity measurements and UV-VIS spectrophotometry. The structural study revealed that CdS: FeS composite thin films are nanocrystalline in nature with hexagonal lattice. The electrical resistivity of CdS: FeS thin film was found to be of the order of 10^6 Ωcm. The thermo-emf measurement conforms n-type conductivity of CdS: FeS thin film.The optical characterization shows that the band gap of the spray deposited CdS: FeS thin film is 2.34 eV.

Key Words: *Thin Films, Nanostructures, Structural Properties, Electrical Properties*

INTRODUCTION
The development of high speed micro and nano devices demands novel nanostructured materials with improved physical and chemical properties. The physical and chemical properties of the material can be engineered as per need by preparing various kinds of multicomponent chalcogenide thin films (Valkonen *et al.,* 1998; Edamura and Muto, 1995). In recent years the ternary metal chalcogenide thin films were found suitable in the development of various fields such as microelectronics, communication, optical electronics, catalysis, and energy conservation devices (Kuku *et al.,* 2006). In this regard, there has been increasing interest in the synthesis of nanocrystalline ternary semiconducting composite materials, such as CdS-ZnS, CdS-Bi_2S_3, $CuInSe_2$, $Cu(In_{1-x}Al_x)Se_2$, $(NiS)_x(CdS)_{(1-x)}$ etc. (Nicolau *et al.,* 1990; Ahire *et al.,* 2001; Pathan and Lokhande, 2005; Dhanam *et al.,* 2010; Ubale and Bargal, 2011; Khare, 2012; Khare *et al.,* 2012; Chate *et al.,* 2011). They offer the great opportunity to modify the electrical and optical properties as per demand into a single semiconductor composite material, which provides many potential applications in the field of semiconductor spintronic and optoelectronic devices (Wu, 2006). The electrical, optical and magnetic properties of CdS are strongly modified by the doping of Fe (Mycielski *et al.,* 1986; Sarem *et al.,* 1990). In the present work prepared CdS: FeS thin films were well characterized using X-ray diffractometer (XRD), two point dc resistivity measurement technique and UV-VIS spectrophotometry.

MATERIALS AND METHODS
Spray pyrolysis is a versatile and effective technique to deposit wide variety of nanostructured metal oxide (Ubale and Ibrahim, 2011; Ubale and Deshpande, 2010), metal chalcogenides (Misho *et al.,* 1991; Lopez *et al.,* 1996) and selenides (Mangalhara *et al.,* 1988; Weng and Cocivera, 1992) thin films. To deposit CdS: FeS thin films onto glass substrates by spray pyrolysis technique ferric chloride, cadmium chloride and thiourea supplied by Sd-fine Chemicals, Mumbai were used. The transparent yellowish orange coloured spray solution of stable phase was prepared by mixing 10 mL of 0.1M ferric chloride, 10 mL of 0.1M cadmium chloride and 20 mL of 0.1M thiourea in a measuring cylinder. This solution was sprayed using compressed air as a carrier gas onto hot glass substrates kept at 573 ±5K temperature.

Several trials were conducted to optimize the different deposition parameters such as substrate temperature, spray rate, concentrations of cationic and anionic sources etc.
In the present work, thickness of the film was measured by gravimetric weight difference method using the relation,

$$t = \frac{m}{\rho \times A} \quad (1)$$

where, 'm' is the mass of the film deposited on the substrate in gram; 'A' is the area of the deposited film in cm^2 and 'ρ' is the density of the deposited material in bulk form. The structural studies were carried out using Philips PW 1710 diffractometer, with Cu-Kα radiation of wavelength 1.5405 A°. The dc two-point probe method of dark electrical resistivity was used to study the variation of resistivity with temperature. The optical characteristics were studied using Lambda 25 UV-VIS spectrophotometer (PerkinElmer) to find band gap energy of CdS: FeS thin films.

RESULTS AND DISCUSSION

Structural Studies

The crystal structure of CdS: FeS thin films deposited by spray pyrolysis method have been carried out by means of X-ray diffraction analysis in the range of 2θ between 10 to 90^0 . A typical XRD peak pattern of CdS: FeS films of thickness 251 nm deposited onto glass substrate is shown in Figure 1. The XRD peaks in the pattern at (0 0 2), (2 1 1) and (2 1 7) confirms hexagonal structure [JCPDS card CdS: 80-06, 6-314 and FeS:80-1026,1027,1029]. The average crystallite size of the film was determined by using Debye Scherrer formula,

$$d = \frac{0.9\,\lambda}{\beta \mathrm{Cos}\ \theta} \quad (2)$$

where 'λ' is the wavelength used (0.154 nm); 'β' is the angular line width at half maximum intensity in radians; 'θ' is the Bragg's angle. The average particle size calculated from the prominent peaks (0 0 2) and (2 1 1) is 26.34 nm, which shows that spray deposited CdS: FeS thin films nanocrystalline in nature.

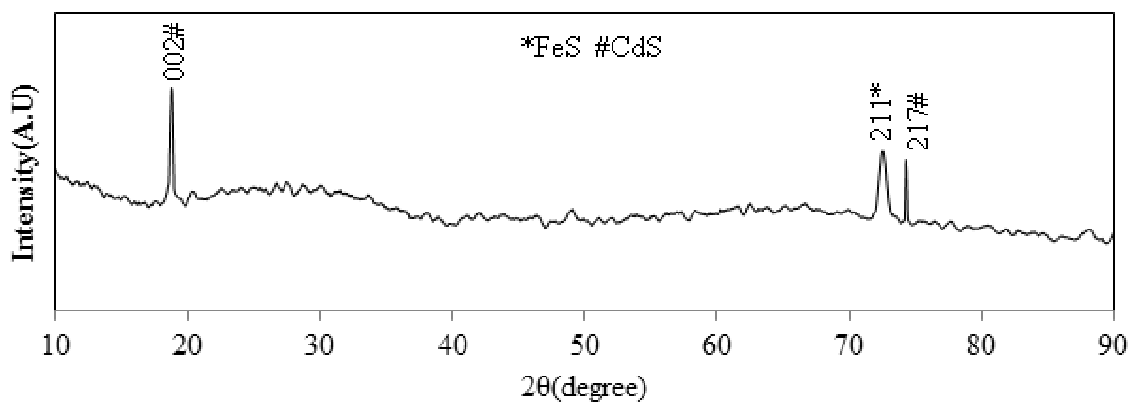

Figure 1: XRD pattern of composite spray deposited CdS: FeS thin film

Electrical Properties

The variation of dc-electrical resistivity with temperature was studied for CdS: FeS thin film in the temperature range 300 to 483 K. The room temperature electrical resistivity is of the order of 10^6 Ωcm. It was observed that resistivity decreases as the film temperature increases which shows that CdS: FeS films are semiconducting in nature. Figure 2 shows variation of log (ρ) with reciprocal of temperature (1/T) for CdS: FeS thin films. The dependence of resistivity on temperature is almost linear indicating the presence of only one type of conduction mechanism in the film.
The thermal activation energy was calculated using the relation,

$$\rho = \rho_0 \exp^{(E_0/KT)} \quad (2)$$

where, ρ is resistivity at temperature T, ρ_0 is a constant; K is Boltzmann constant. The activation energy (E_0) was calculated from the resistivity plots. The activation energy is found 0.045eV.The thermo-emf developed across hot-cold junction of CdS: FeS thin film in dark was measured as a function of temperature difference. The polarity of the generated thermo-emf was negative at the cold end with respect to the hot end, which confirms that, CdS: FeS thin films are of n-type.

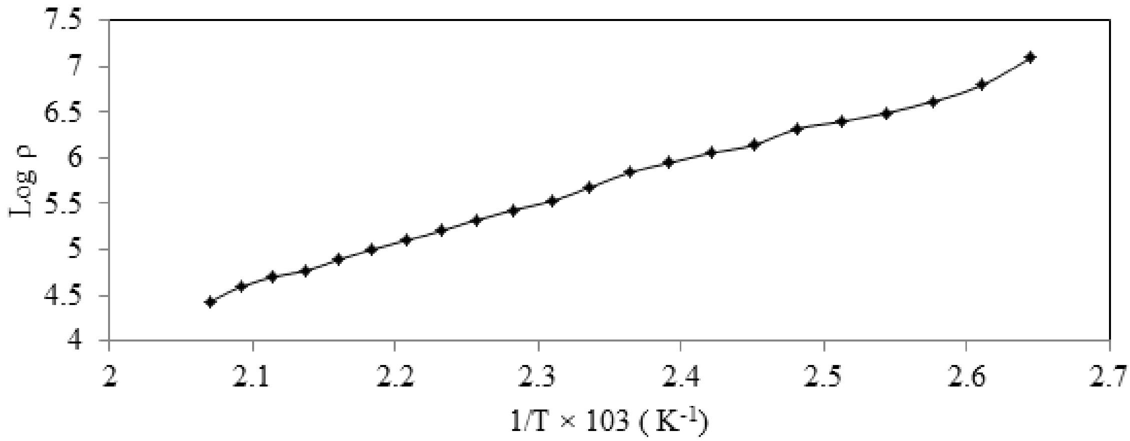

Figure 2: Variation of Log of resistivity with 1/T for CdS: FeS thin film

Optical Properties

The optical absorption studies were carried out in the wavelength range 380 to 1100 nm and the absorption spectra is analyzed to find band gap energy of CdS: FeS thin film.

Figure 3 shows the variation of optical absorbance (αt) of CdS: FeS thin film with wavelength deposited onto glass substrate, here 't' is film thickness and 'α' is the optical absorption coefficient.

The nature of transition is determined by using the relation,

$$\alpha = \frac{A(h\upsilon - Eg)^n}{h\nu} \qquad (3)$$

where hν is the photon energy, E_g is the band gap energy, A and n are constants. For allowed direct transitions n = 1/2 for allowed indirect transitions n = 2.

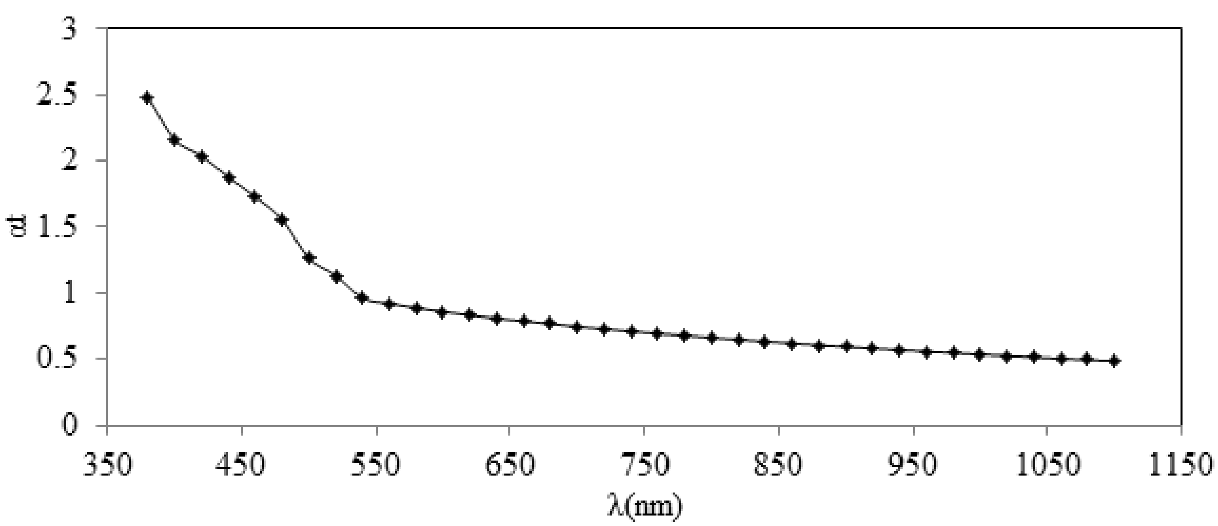

Figure 3: Variation of optical absorption vs. wavelength for CdS: FeS thin film

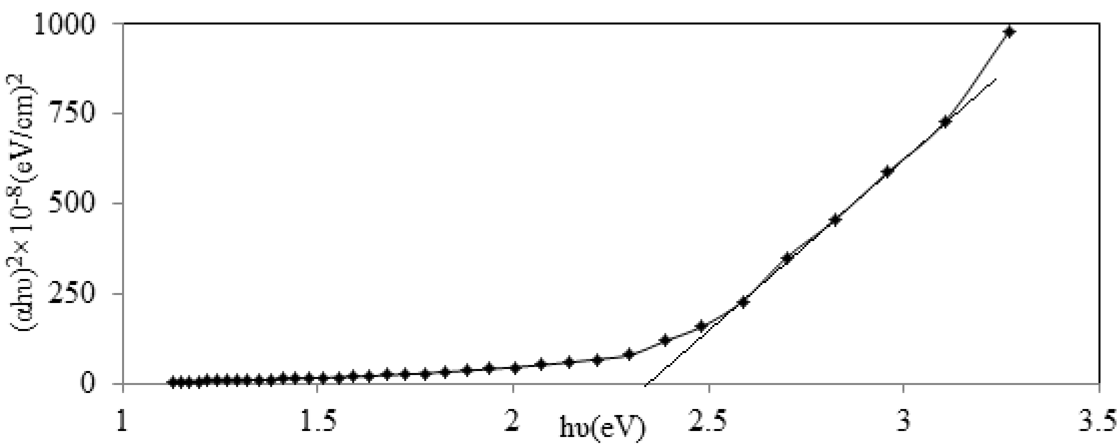

Figure 4: Variation of $(\alpha h\upsilon)^2$ verses hυ for CdS: FeS thin film

The plot of $(\alpha h\nu)^2$ versus hν is shown in Figure 4. The nature of plot indicates the existence of direct transition. The optical band gap energy "Eg" is determined by extrapolating the straight line portion to the energy axis for zero absorption coefficients. The value of Eg for as deposited CdS: FeS thin film is found 2.34 eV.

Conclusion

CdS: FeS thin films were successfully deposited onto glass substrates by spray pyrolysis method by using aqueous solutions of ferric chloride, cadmium chloride and thiourea at 573K temperature. XRD measurement confirms that CdS: FeS thin films are nanocrystalline in nature withhexagonal phase.The electrical characterization shows that CdS: FeS thin films are semiconducting in nature with n-type conductivity. The optical characterization shows that the band gap of the spray deposited CdS: FeS thin film is 2.34 eV.

REFERENCES

Valkonen MP, Lindroos S and Leskela M (1998). $Cd_xZn_{1-x}S$ solid solution thin films, CdS thin films and CdS/ZnS multilayer thin films grown by SILAR technique. *Applied Surface Science* **134**(1-4) 283-291.

Edamura T and Muto J (1995). Electrode position of zinc cadmium sulphide thin films from acidic aqueous electrolyte solution at room temperature. *Journal of Materials Science Letters* **14**(12) 889-891.

Kuku TA, Azi SO and Osasona O (2006). Electrical properties of vacuum evaporated $PbSnS_3$ thin films. *Journal of Materials Science Letters* **41**(4) 1067-1071.

Nicolau YF, Dupuy M and Brunel M (1990). ZnS, CdS, and $Zn_{1-x}Cd_xS$ Thin Films Deposited by the Successive Ionic Layer Adsorption and Reaction Process. *Journal of the Electrochemical Society* **137**(9) 2915-2924.

Ahire RR, Sankapal BR and Lokhande CD (2001). Photoelectrochemical characterization of chemically deposited $(CdS)_x(Bi_2S_3)_{1-x}$ composite thin films. *Materials Chemistry and Physics* **72**(1) 48-55.

Pathan HM and Lokhande CD (2005). Chemical deposition and characterization of copper indium diselenide (CISe) thin films. *Applied Surface Science* **245**(1-4) 328-334.

Dhanam M, Kavitha B and Velumani S (2010). An investigation on silar $Cu(In_{1-x}Al_x)Se_2$ thin films. *Materials Science and Engineering: B* **174**(1-3) 209-215.

Ubale AU and Bargal AN (2011). Characterization of nanostructured photosensitive $(NiS)_x(CdS)_{1-x}$ composite thin films grown by successive ionic layer adsorption and reaction (SILAR) route. *Materials Research Bulletin* **46**(7) 1000-1010.

Khare A (2012). Factors affecting the electro-optical and structural characteristics of nano crystalline Cu doped (Cd–Zn)S films. *Journal of Physics and Chemistry of Solids* **73**(7) 839-845.

Khare A, Sahu RB and Sharma SK (2012). Effect of NaF on optical and structural properties of $Cd_xZn_{1-x}S$ nano crystalline films. *Optik-International Journal for Light and Electron Optics* **123**(13) 1133-1137.

Chate PA, Sathe DJ and Hankare PP (2011). Growth and characteristics of Zn–Se–S thin layers by dip method. *Journal of Alloys and Compounds* **509**(39) 9425-9427.

Wu XJ (2006). p-type conductivity and donor-acceptor pair emission in $Cd_{1-x}Fe_xS$dilute magnetic semiconductors. *Applied Physics Letter* **89**(26) 262118.

Mycielski A, Dzwonkowski P, Kowalski P, Kowalski BJ, Orlowski BA, Dobrowolska M, Arciszewska M, Dobrowolaski W and Baranowski JM (1986). Location of the Fe^{2+} ($3d^6$) donor in the band structure of mixed crystals $Hg_{1-v}Cd_vSe$. *Journal of Physics C: Solid State Physics* **19**(19) 3605-3613.

Sarem A, Kowalski BJ and Orlowski BA (1990). Optical properties of Fe-based semimagnetic semiconductors. *Journal of Physics: Condensed Matter* **2**(41) 8173-8187.

Ubale AU and Ibrahim SG (2011). Effect of acetic acid complex on physical properties of nanostructured spray deposited $FeCdS_3$ thin films. *Journal of Alloys and Compounds* **509**(5) 2364-2367.

Ubale AU and Deshpande VP (2010). Effect of manganese inclusion on structural, optical and electrical properties of ZnO thin films. *Journal of Alloys and Compounds* **500**(1) 138-143.

Misho RH, Murad WA and Salmin ZAR (1991). Optical properties of two structures of Bi_2O_3 and BiS_2 thin films prepared by the method of chemical spray pyrolysis. *Solar Energy Materials* **21**(4) 347-358.

Lopez S, Granados S and Ortiz A (1996). Spray pyrolysis deposition of Sn_2S_3thin films. *Semiconductor Science and Technology* **11**(3) 433-436.

Mangalhara JP, Thangraj R and Agnihotri OP (1988). Photoelectrochemical conversion using sprayed CdSe. *Bulletin of Materials Science* **10**(4) 333-340.

Weng S and Cocivera M (1992). Thin-Film Cadmium Selenide Prepared from Cadmium Oxide Formed by Spray Pyrolysis. *Journal of the Electrochemical Society* **139**(11) 3220-3224.

.