

Structural, Electrical and Optical Properties of Nanostructured FeCdS₃ Thin Films Deposited by Chemical Spray Technique: Effect of Complex

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Abstract Structural, optical and electrical properties of nanostructured FeCdS₃ thin films deposited by spray pyrolysis method using ferric nitrate and cadmium chloride as cationic and thiourea as anionic source with complexes EDTA, tartaric acid and acetic acid is reported. The structural and morphological studies were carried out using X-ray diffractometry (XRD), energy dispersive X-ray analysis (EDS) and scanning electron microscopy (SEM). The X-ray spectrum reveals that the films are nanocrystalline in nature with mixed orthorhombic and hexagonal phase due to FeS₂ and CdS lattice. The SEM study shows that the surface morphology of the film is highly influenced by the complexing agent used in the deposition process. Also the optical absorption and electrical resistivity measurements show that the band-gap and activation energy of FeCdS₃ thin films varies from 2.45 to 2.63 eV and 0.09 and 0.38 eV respectively depending on the complex used.

Keywords Thin Films, Nanostructures, Chemical Synthesis, Electrical Properties, Optical Properties

1. Introduction

Recently preparation of nanostructured materials by cost effective chemical method and investigation of their physical properties is an emerging field of research. The development of nanotechnology is highly influenced by the various chemical and physical deposition processes as the particle size of the nanomaterial is dependent on the deposition method as well as its different preparative parameters. These materials have indeed become a very active research field in the areas of solid state physics, solid state chemistry, materials engineering and medical sciences. The nanostructured materials differ from conventional polycrystalline materials by the particle size that composes them and they show properties that are significantly different from those of conventional material as a result of the large surface area, which controls its bulk properties. If particles have dimensions comparable to the wavelength of electrons, phonons etc., inside the material, quantum mechanical effects plays important role in changing their physical properties especially electrical, magnetic and optical[1]. A blue-shift in optical spectra of quantum-confined particles, and an increase in luminescent efficiency of semiconductors make them suitable for various semiconductor devices. In

addition nanostructured materials show lower melting temperatures and higher catalytic activity. The nanostructured materials show potential applications in organic solar cells, rechargeable solid state batteries, fuel cells, molecular electronics, single-electron devices, scanning probes, and sensors[2-6]. Thin films of transition metal chalcogenides particularly Fe and Cd chalcogenides have received much attention due to their importance in photovoltaic and optoelectronic semiconductor devices, as they fulfil some of the requirements that are essential for device fabrication[7-9]. Recently pyrite (FeS₂) has attracted attention due to its electronic properties. The p-type pyrite films show n-type conduction after addition of dopants, such as Ti[10], Co[11], Ni[12] and Cu[13]. CdS is another metal chalcogenide, which is most popularly employed heterojunction partner to p-CdTe due to its similar chemical properties useful in achieving high solar conversion efficiencies[14-17]. However, ternary chalcogenide semiconductors Zn_{1-x}Cd_xSe[18], (HgS)_x(Bi₂S₃)_{1-x}[19], Zn_{1-x}Fe_xSe[20], Zn_{1-x}Fe_xS[21], Cd_{1-x}Fe_xSe[22], PbS-Cu_xS[23], Bi₂S₃-Cu_xS[24,25], Cd_{1-x}Zn_xS[26-28] have attracted interest of many researchers as their energy gap can be adjusted depending on composition which is useful to improve optoelectronic and photovoltaic characteristics[29]. Wu X. J. et al[30] have prepared Cd_{1-x}Fe_xS thin films by MOCVD and found that with increasing Fe content in the Cd_{1-x}Fe_xS thin films, the conductivity of the films could possibly reverse from n-type to p-type. Although many work on Cd_{1-x}Fe_xS thin film have reported previously, but no reports were available on

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FeCdS₃ or CdS-FeS₂ thin films yet by spray method[31,32]. Several chemical techniques have been reported for the preparation of binary and ternary chalcogenide thin films, namely chemical bath deposition[33], spray pyrolysis[34], successive ionic layer adsorption and reaction[35], electrodeposition[36], thermal evaporation[37] and sol gel[38] etc. Out of these techniques, the spray pyrolysis is an economic and popular method as it is simple and safe[39]. One interesting feature of spray pyrolysis is that, under specific conditions the preparation of composite thin films can easily be achieved by adjusting the composition of spray solution. From the industrial point of view, synthesis of nanostructured materials at temperature below 773 K by chemical spray pyrolysis method can have wide scope as does not require sophisticated instruments such as vacuum systems. Generally, the starting chemicals are commonly available metal chlorides and nitrates, which are very cheap. The preparative parameters deposition-temperature, spray rate and solution concentration can be easily optimised to get good quality films.

In this paper, we present the synthesis of FeCdS₃ thin films using spray pyrolysis method. The effect of complexing agents on structural, morphological, optical and electrical properties of spray-deposited FeCdS₃ thin films is been discussed.

2. Experimental Details

Spray pyrolysis is essentially a thermally stimulated reaction between clusters of ions or atoms of different chemical species. In spray technique a solution (usually aqueous) containing soluble salts of the constituent atoms of the desired compound is sprayed on a substrate maintained at elevated temperatures. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal, cluster, or crystallites of the product. To deposit FeCdS₃ thin films onto glass substrates by spray pyrolysis technique ferric nitrate, cadmium chloride, thiourea, EDTA, tartaric acid and acetic acid are used. The film growth rate depends on the number of parameters like temperature of the substrate, duration of spray, the solution spray rate and pH of the solution. The ferric nitrate, thiourea and cadmium chloride powders supplied by Sd-fine Chemicals, Mumbai were dissolved in distilled water to prepare different solutions. The 10 ml volume of 0.1M ferric nitrate, 0.1M CdCl₂ and 0.1M thiourea each were mixed directly to get transparent yellowish orange coloured solution of stable phase. In this solution, 10 ml of 0.1M one of the complexing agent from EDTA, tartaric acid and acetic acid was added to prepare spray solution. Finally, the solution was sprayed using compressed air as a carrier gas onto hot glass substrates kept at 453 ±5K temperature. Several trials were conducted to optimize the different deposition parameters such as substrate temperature, spray rate, concentration of zinc acetate etc. The optimized deposition temperature was 453K; the films deposited below this temperature were discontinuous

and less adhesive. In addition, the optimized spray rate was found out 6 c.c min⁻¹. All these optimized preparative parameters given in Table 1.

Table 1. Optimized preparative parameters for FeCdS₃ film deposition

| Name of Parameter | Optimized value |
|--|---|
| Chemical composition of spray solution | 10 ml, 0.1 M Ferric Nitrate + 10 ml, 0.1M CdCl ₂ + 10 ml, 0.1 M thiourea + Complexing agent. |
| Nature of substrate | Amorphous glass |
| Substrate temperature | 453 ±5K |
| Spray rate | 6 ml /min |
| Spray nozzle diameter | 0.5 mm |
| Spray nozzle to Substrate distance | 28 cm |

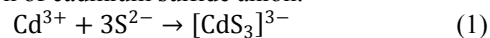
The average thickness of the film was measured by the gravimetric and Fizzau's method. The two-point dc probe method of dark electrical resistivity was used to study the variation of resistivity with temperature. A copper block with heating arrangement was used as a sample holder cum heater along with chromel–alumel thermocouple to measure the temperature. The structural studies were carried out using Philips PW 1710 diffractometer, with Cu-Kα radiation of wavelength 1.5405 Å. The optical characteristics were studied using Hitachi 330 spectrophotometer to find band gap energy. The surface morphological studies were carried out using JSM-6360 scanning electron microscope. The FTIR spectra of the films were recorded using Shimadzu IR Affinity-1 instrument.

3. Result and Discussion

3.1. Film Deposition

Cd³⁺ and S²⁻ ions interact to form [FeCd₃]³⁻ anion which attack on Fe³⁺ ions from spray solution at 453K temperature on hot substrate to form FeCdS₃. The growth of FeCdS₃ film on hot substrate takes place in two steps.

(a) Formation of cadmium sulfide anion:

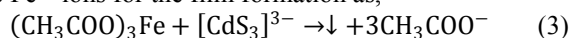


(b) Attack of Fe³⁺ ions on [CdS₃]³⁻ to produce FeCdS₃:

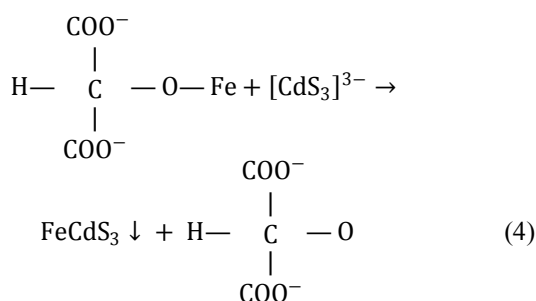


The effect of various carrier ions has been studied by using acetic acid, tartaric acid and EDTA on the rate of FeCdS₃ film formation. It is observed that the rate of reaction (2) is governed, by the presence of complexing anion, which acts as a carrier as well as controller for release of Fe³⁺ ions. The carrier ion carries Fe³⁺ ions by complexation and releases at the proper site to form FeCdS₃.

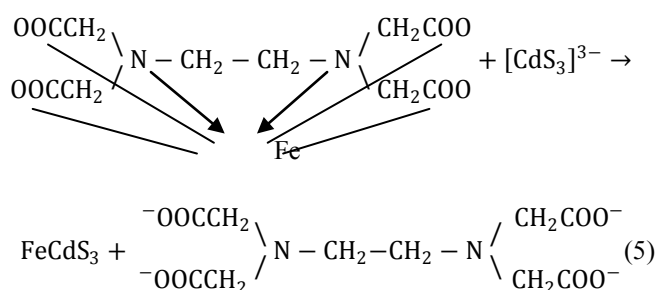
(i) In presence of acetic acid: When acetic acid is used iron acetate complex is formed which decomposes rapidly to liberate Fe³⁺ ions for the film formation as,



(ii) In presence of tartaric acid: When tartaric acid is used iron tartarate complex is formed which decomposes slowly to liberate Fe³⁺ ions for the film formation as,



(iii) In presence of EDTA: When ethylene diamine tetra acetic acid is used iron forms highly stable Fe-EDTA complex which decomposes very slowly to liberate Fe^{3+} ions for the film formation as,



3.2. Structural Analysis

Figure 1 shows the X-ray diffraction spectra of FeCdS_3 films deposited using various complexing agents. From the XRD patterns it can be seen that the films deposited using complex tartaric acid are amorphous (sample C), whereas for other complexes films are polycrystalline. Addition of tartaric acid into the spray solution forms iron tartarate complex. The structure of this anion depends upon the ionization level of tartaric acid. The structure of the iron tartarate anion will be different for different ionization levels. For tartaric acid, Fe and Cd complex may be in its fully ionised form, which forms a very strong chelete ring, which thermally decomposes at slow rate that produces amorphous phase of FeCdS_3 . The EDTA is a powerful chelating agent which forms stable complex with metal ions i.e. Fe-EDTA complex which liberates Fe^{3+} ions at slower rate and provides much time to deposit highly oriented phases in (110) and (203) direction due to FeS_2 and CdS respectively. However when acetic acid is used the Fe-actate rapidly decomposes which produces nanocrystalline phase of FeCdS_3 . The peaks (110), (020), (120) and (104) are due to orthorhombic and hexagonal phase of FeS_2 and CdS respectively. Some additional peaks (210), (110) and (102) are observed when films were deposited without complexing agent. The comparison of observed and standard data for FeS_2 and CdS is given in Table 2. The grain size of crystallites was calculated by using Scherrer formula,

$$d = \frac{\lambda}{\beta \cos \theta} \quad (6)$$

where λ is the wavelength used (0.154nm); β is the angular line width at half maximum intensity; θ is the Bragg's angle. The grain size for the film deposited using acetic acid is of the order of 11 nm and it increases to 13, 39 nm for the

film deposited without complex and using EDTA.

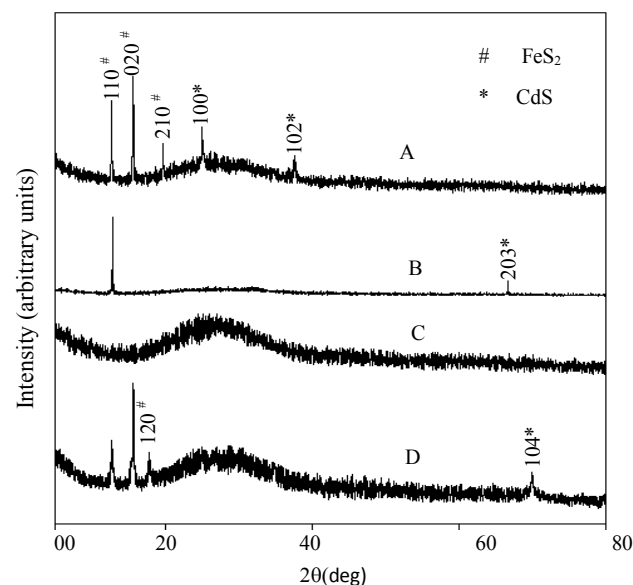


Figure 1. XRD patterns of FeCdS_3 films (A) without Complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

Table 2. Comparison of observed and standard XRD data of FeCdS_3 films. (JCPDS Card No 03-0799, 77-2306)

| Sample | Observed data | | Standard JCPDS data | | hkl | Phase |
|--------------------------|---------------|----------------------|---------------------|----------------------|-----|----------------|
| | 2 θ | d (\AA^0) | 2 θ | d (\AA^0) | | |
| Without Complexing agent | 11.738 | 3.446 | 11.835 | 3.440 | 110 | FeS_2 |
| | 15.058 | 2.754 | 15.039 | 2.710 | 020 | FeS_2 |
| | 19.914 | 2.069 | 19.925 | 2.050 | 210 | FeS_2 |
| | 24.927 | 3.555 | 24.837 | 3.581 | 100 | CdS |
| | 36.608 | 2.459 | 36.662 | 2.449 | 102 | CdS |
| EDTA | 11.892 | 3.469 | 11.835 | 3.440 | 110 | FeS_2 |
| | 66.882 | 1.400 | 66.859 | 1.398 | 203 | CdS |
| Tartaric acid | - | - | - | - | - | - |
| Acetic acid | 11.825 | 3.432 | 11.835 | 3.440 | 110 | FeS_2 |
| | 15.069 | 2.720 | 15.039 | 2.710 | 020 | FeS_2 |
| | 17.526 | 2.331 | 17.586 | 2.320 | 120 | FeS_2 |
| | 60.982 | 1.500 | 60.912 | 1.5197 | 104 | CdS |

3.3. Morphology

The SEM micrographs of FeCdS_3 films deposited using various complexes are shown in Fig. 2. From SEM images, it is observed that the deposited FeCdS_3 films are uniform, without cracks with dense surface morphology that covers entire substrate surface area. The SEM images of films deposited without complex and using EDTA shows web-like architecture of FeCdS_3 with some irregular grain growth on web structure. Films deposited from tartaric acid complex revealed homogenous dense amorphous morphology with randomly oriented tiny needle like grains. However, the films deposited using acetic acid complex shows vertical rod-like architecture of FeCdS_3 nano-grains, which show extremely different morphology as compared to the films, deposited at other conditions. To study stoichiometry of the film quantitative analysis was carried out using the EDAX technique. Figure 3 shows a typical EDAX pattern of the FeCdS_3 film deposited on the glass substrate from acetic acid

complex. The elemental analysis was carried out only for Fe, Cd and S; the average atomic percentage of Fe:Cd:S was 22:19:59 showing slight cadmium deficiency.

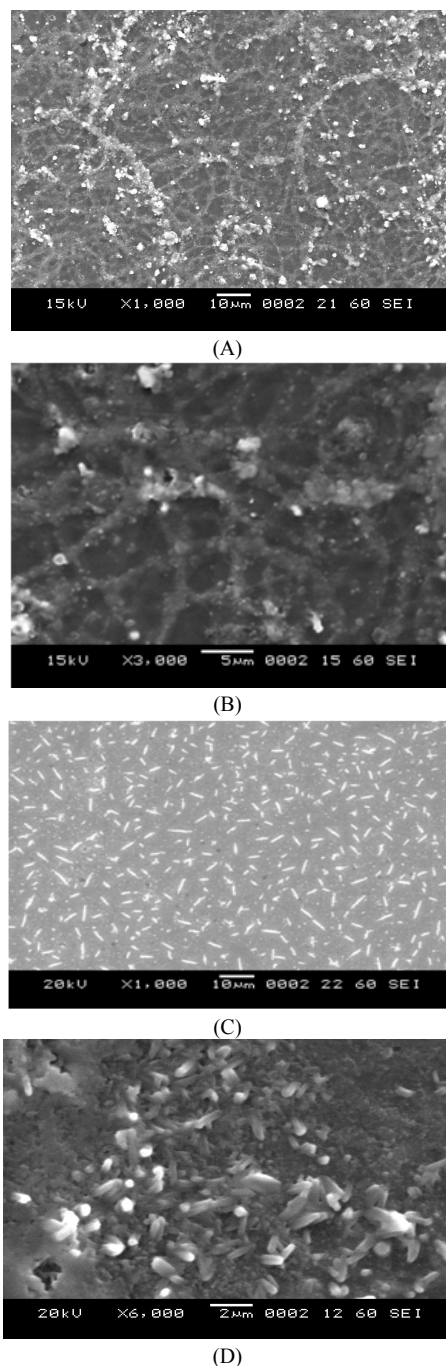


Figure 2. SEM images of FeCdS₃ films: (A) without Complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

3.4. Electrical Analysis

In the present work in order to investigate electrical characteristics silver paste was used to make ohmic contacts to FeCdS₃ thin film. The nature of contact was checked up to 30 V by two-probe method. The I-V characteristic of FeCdS₃/Ag contacts are shown in figure 4. The I-V characteristics for films are found to be linear which shows that silver produces ohmic contact with FeCdS₃.

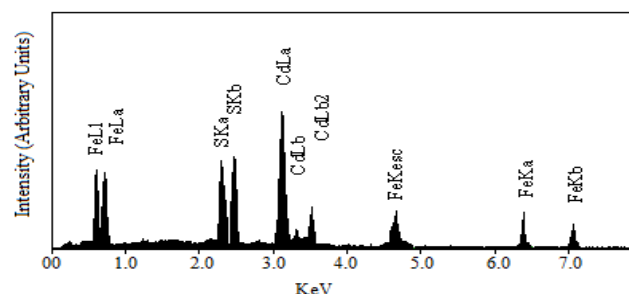


Figure 3. EDAX spectrum of as deposited FeCdS₃ thin film

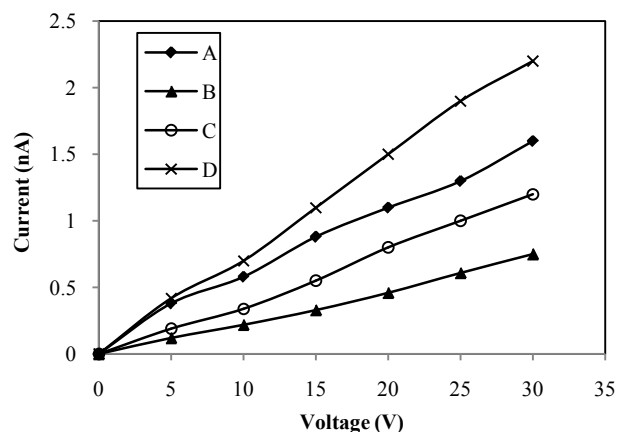


Figure 4. I-V characteristic FeCdS₃ films: (A) without complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

Variation of DC-electrical resistivity with temperature was studied for FeCdS₃ thin film deposited from various complexing agents in the temperature range 309 to 423 K. It was observed that resistivity decreases as the film temperature increases which shows that FeCdS₃ films are semiconducting. Figure 5 shows variation of log (ρ) with reciprocal of temperature ($1/T$) for FeCdS₃ films.

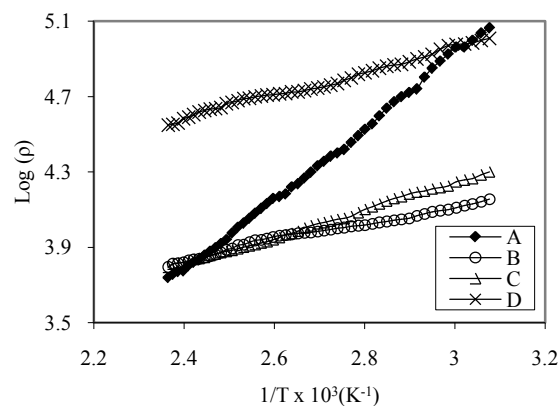


Figure 5. Variation of Log of resistivity with $1/T$ for FeCdS₃ films: (A) without Complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

The resistivity of the film deposited using EDTA and tartaric acid is quite less as that of the film deposited from acetic acid. However, the film deposited without complexing agent shows much variation in resistivity when temperature was changed from 309 to 423 K (Table 3). This change in resistivity may be attributed to change in the density of free electrons and change in mechanism of scattering at the surface of nanostructured films due to grain boundaries.

Table 3. Variation of FeCdS₃ thin film thickness, band-gap energy, activation energy and resistivity with complexing agent used for preparation

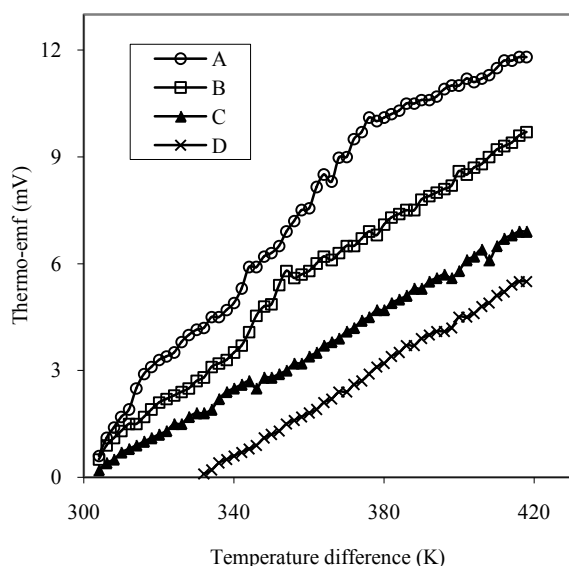
| Sample | Complex used | Film thickness (nm) | Band- gap energy (eV) | Activation energy (eV) | 10 ³ × ρ (Ω-cm) | |
|--------|---------------|---------------------|-----------------------|------------------------|----------------------------|---------|
| | | | | | at 309K | at 423K |
| A | - | 138 | 2.46 | 0.38 | 27.28 | 0.55 |
| B | EDTA | 129 | 2.63 | 0.09 | 1.84 | 0.62 |
| C | Tartaric Acid | 145 | 2.54 | 0.14 | 2.52 | 0.62 |
| D | Acetic Acid | 136 | 2.45 | 0.12 | 12.54 | 3.53 |

The thermal activation energy was calculated using the relation,

$$\rho = \rho_0 e^{\left(\frac{E_0}{KT}\right)} \quad (7)$$

where, ρ is resistivity at temperature T, ρ₀ is a constant; K is Boltzmann constant. The activation energy (E₀) was calculated from the resistivity plots. The activation energy is of the order of 0.38 eV for the film deposited without complexing agent and it decreases when complex is used. (table 3). The activation energy of the film deposited using EDTA complex is minimum (0.09eV), it may be due to improved crystal structure.

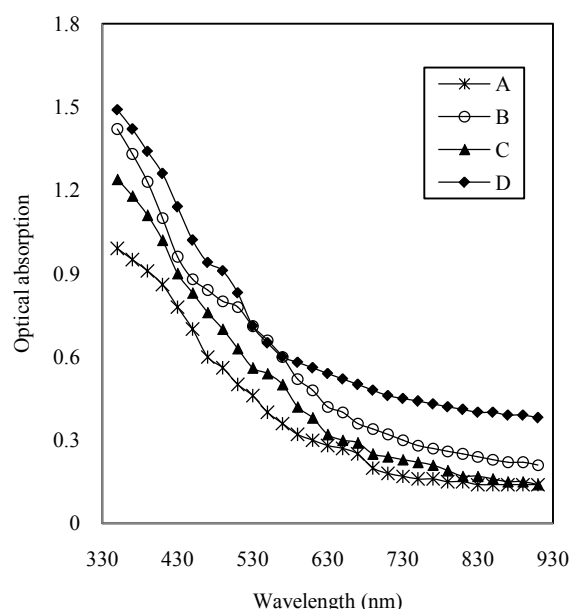
The TEP for FeCdS₃ films was measured as a function of temperature in dark in the temperature range 304 to 418 K (Figure 6). The polarity of the generated thermo-emf was negative at the cold end with respect to the hot end, which confirms that FeCdS₃ films are of n-type.

**Figure 6.** Variation of thermo emf (mV) with temperature difference for FeCdS₃ films: (A) without complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

3.5. Optical Properties

The optical absorption studies were carried out in the wavelength range of 350 to 910 nm and the absorption spectra is analysed to find band gap energy of FeCdS₃. Figure 7 shows the variation of optical absorbance (αt) of FeCdS₃ films deposited from various complexes, here 't' is film thickness and 'α' is the optical absorption coefficient.

The variation in absorbance observed is attributed to the film thickness, at what extent film is crystallized, the pinhole free surface and the voids in the film. The film deposited from acetic acid shows more absorbance which may be due availability of more surface area as seen in SEM image.

**Figure 7.** Variation of optical absorption vs. wavelength FeCdS₃ films: (A) without complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

The nature of transition is determined by using the relation,

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}, \quad (8)$$

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.

The width of the energy gap is a characteristic value for each material. The plots of (αhν)² versus hν are shown in Figure 8. The nature of plots indicates the existence of direct transition. A finite energy shift in the absorption edge of the nanocrystalline material is generally expected towards higher energy side in the spectrum as that of bulk counterpart. The films deposited without complex and deposited using tartaric and acetic acid has band gap energy of the order of 2.45eV however, deposited from EDTA complex has band gap 2.63 eV (table 3). This change may be due to dependence of the density of states in a band on the number of atoms and disorders in a nanostructured semiconductor, which is more

in nano-size thin films as they are strongly affected by the dimensions of the material. Similar red shift in the band-gap energy with thickness has been reported for chemically deposited thin films[40, 41].

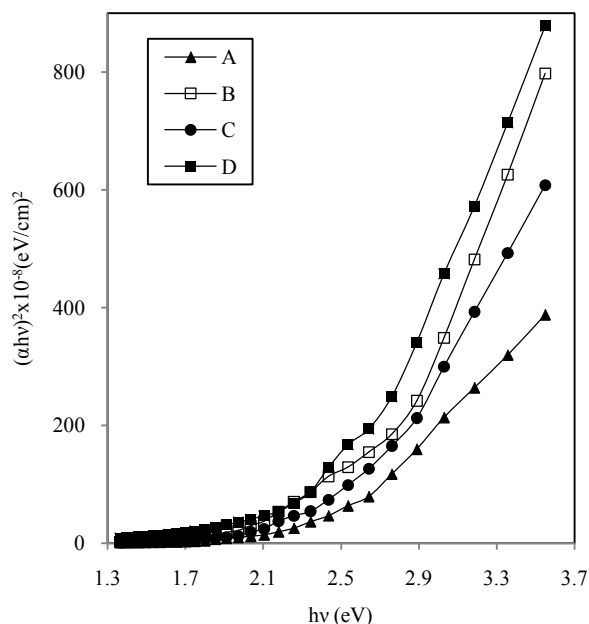


Figure 8. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ of FeCdS₃ films: (A) without complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

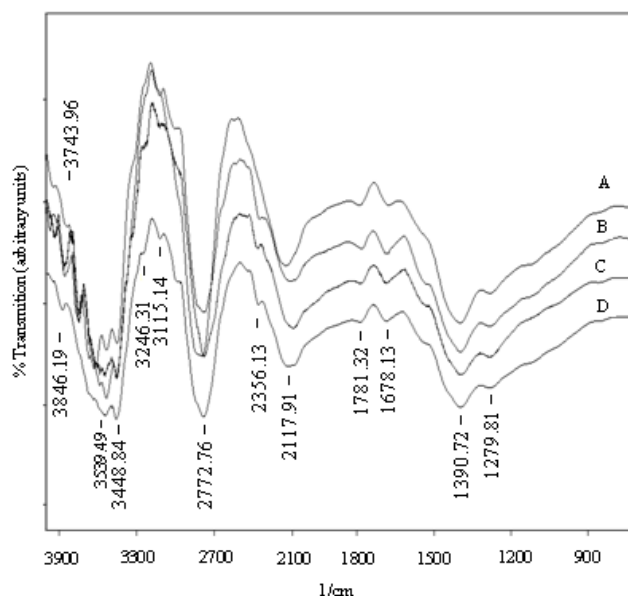


Figure 9. FTIR spectra of FeCdS₃ films: (A) without complexing agent, (B) EDTA, (C) Tartaric acid and (D) Acetic acid

The FTIR spectra of the films deposited with and without complex shows no remarkable change that confirms saturation behaviour of the chemical reaction (Figure 9). It shows that stoichiometry of FeCdS₃ is maintained for both the films deposited without and with complex. The low intensity bands observed for acetic acid induced FeCdS₃ is in conformity with the stable film formation i.e. improved grain growth; whereas gradual increase in percentage transmission

of FeCdS₃ sample prepared using EDTA, tartaric acid and without carrier ions is in support of the fact that nature of FeCdS₃ film is governed by presence and absence of carrier ions. With acetate ions the film formed must be regular and contains more nanocrystalline phase compared to other films prepared with other carrier ions, which is also in support with SEM analysis. The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for types of bonds. The absorptions at 3846 and 3743 cm⁻¹ indicates N-H stretch. An absorption above 3000 cm⁻¹ indicates C=C, either alkenes or aromatic. The O-H or N-H absorption between 3115 and 3539 cm⁻¹ indicates an alcohol, N-H containing amine or amide, or carboxylic acid. The Si-H stretch is observed at 2356 cm⁻¹. The carbonyl (C=O) absorption band between 1678-1781 cm⁻¹ indicates either an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide. The C-O absorption between 1279 and 1390 cm⁻¹ are normally rounded like the O-H and N-H peak and are prominent. A broad bend observed in between 2356 to 3539 cm⁻¹ may be due to strong hydrogen bonding.

5. Conclusions

In the present paper, synthesis of nanostructured FeCdS₃ thin films by chemical spray pyrolysis technique with and without complex is discussed. The structural, electrical and optical properties of nanostructured FeCdS₃ films were investigated. The XRD pattern suggests that the FeCdS₃ films are nanocrystalline in nature with mixed orthorhombic and hexagonal phase of FeS₂ and CdS. SEM micrograph shows that, the films deposited using acetic acid and EDTA complex shows vertical rod-like and web-like architecture of FeCdS₃. Analysis of UV/VIS spectra of the films reveals that the material is direct semiconductor with band gap in the range 2.45 to 2.63 eV depending on complex used. The thermo-emf measurement confirms that the deposited FeCdS₃ films are of n-type. The resistivity of FeCdS₃ is of the order of 10³ to 10⁴ Ω-cm at 309 K depending on complex used for deposition.

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REFERENCES

- [1] A.J.A. Wurmubst, M.M.R. Boutz., "Superplastic deep drawing of tetragonal zirconia ceramics at 1160°C", J. European Cer. Soc. Vol. 18, pp.2101-2108, 1998.
- [2] A. Aviram, M. A. Ratner, "Molecular rectifiers", Chem. Phys. Lett. Vol. 29, pp.277-283, 1974.

- [3] F.L. Carter, R.E. Siatkowsky, H. Woliltjen, *Molecular Electronics Devices*, North Holland, Amsterdam, 1988.
- [4] A. Aviram (Ed.), *Molecular Electronics Science and Technology*, AIP Coiif. Proc, pp. 262, 1992.
- [5] A.S. Edelstein and R.C. Cammarata, *Nanomaterials: Synthesis, Properties and Applications*, Institute of Physics Publishing, Bristol, 1996.
- [6] Bezryadin, C. Dekker and G. Schmud, "Electrostatic trapping of single conducting nanoparticles between nanoelectrodes," *Appl. Phys. Lett*, Vol. 71, pp. 1273-1275, 1997.
- [7] H. Moon, A. Kathalingam, T. Mahalingam, J.P. Chu and Y.D. Kim, "Studies on electrosynthesized zinc mercury selenide alloys", *J. Mater. Sci. Mater. Electron.*, Vol. 18, pp 1013-1019, 2007.
- [8] S.K. Deskmukh, A.V. Kokate, and D.J. Sathe, "Studies on electrodeposited $Cd_{1-x}Fe_xS$ thin films", *Mater. Sci. Eng.*, Vol. B 122, pp. 206-210, 2005.
- [9] R. Chandramohan, T. Mahalingam, J.P. Chu and P.J. Sebastian, *Solar Energ. Mater. Solar Cells*, "Preparation and characterization of semiconducting $Zn_{1-x}Cd_xSe$ thin films", Vol. 81, pp 371-378, 2004.
- [10] A. Pascual, P. Diaz-Chao, I.J. Ferrer, C. Sánchez, J.R. Ares, "the growth and doping of Fe/Ti chalcogenide thin films" *Solar Energy Materials and Solar Cells*, vol. 87(1-4), pp. 575-582, May. 2005.
- [11] I. J. Ferrer, C. de la Heras and C. Sanchez "The effect of Ni impurities on some structural properties of pyrite thin films," *J. Phys.: Condens. Matter.*, vol. 7, pp. 2115-19, Nov. 1995.
- [12] I. J. Ferrer, C. de la Heras and C. Sanchez "Physical properties of Cu-doped FeS_2 pyrite thin films," *Appl. Surf. Sci.*, vol. 70/71, pp. 588-590, 1993.
- [13] J. Oertel, K. Ellmer, W. Böhne, J. Röhrich and H. Tributsch, "Growth of n-type polycrystalline pyrite (FeS_2) films by metalorganic chemical vapour deposition and their electrical characterization", *J. Crys. Growth*, Vol. 198-199, pp. 1205-1210, 1999.
- [14] C.K. Graetzel and M. Graetzel, "Hydrogen evolution from the photolysis of alcoholic benzophenone solutions via redox catalysis", *J. Am. Chem. Soc.* Vol. 101, pp. 7741-7743, 1979.
- [15] A. Hagfeldt and M. Graetzel, "Light-Induced Redox Reactions in Nanocrystalline Systems", *Chem. Rev.* vol. 95, pp. 49-68, 1995.
- [16] V.L. Colvin, M.C. Schlamp and A.P. Alivisatos, *Nature*, "Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer", Vol. 370, pp. 354, 1994.
- [17] L. Pavesi, L.D. Negro, C. Mazzoleni, G. Franzo and F. Priolo, "Optical gain in silicon nanocrystals", *Nature*, Vol. 408, pp. 440-444, 2000.
- [18] R. Chandramohan, T. Mahalingam, J.P. Chu and P.J. Sebastian, *Solar Energ. Mater. Solar Cells*, "Preparation and characterization of semiconducting $Zn_{1-x}Cd_xSe$ thin films" Vol. 81, pp 371-373, 2004.
- [19] A.U. Ubale and S.C. Shirbhate, "Electrical, optical and morphological properties of chemically deposited nano-structured $HgS-Bi_2S_3$ composite thin films", *J. Alloys Comp.*, Vol. 497, pp. 228-233, 2010.
- [20] Y.F. Chen, W.C. Chou and A. Twardowski, "Spin-glass-like behaviour of Fe based diluted magnetic semiconductors," *Solid State Commun.*, Vol. 96, pp. 865-869, 1995.
- [21] A.B. Kashyout, A.S. Aricò, G. Monforte, F. Crea, V. Antonucci and N. Giordano, *Solar Energ. Mater. Solar Cells*, "Electrochemical deposition of $ZnFeS$ thin film semiconductors on tin oxide substrates," Vol. 37, pp. 43-53, 1995.
- [22] S. Thanikaikarasan, T. Mahalingam, K. Sundaram, Taekyu Kim, Y.D. Kim and S. Velumani, *Adv. Mater. Res*, Vol. 68, pp. 69-76, 2009.
- [23] P.K. Nair and M.T.S. Nair, "Chemically deposited ZnS thin films: application as substrate for chemically deposited Bi_2S_3 , Cu_xS and PbS thin films," *Semicond. Sci. Technol.*, Vol. 7, pp. 239-241, 1992.
- [24] P.K. Nair, M.T.S. Nair, A. Fernandez and M. Ocampo, "Prospects of chemically deposited metal chalcogenide thin films for solar control applications," *J. Phys. ED Appl. Phys.*, Vol. 22, pp. 829, 1989.
- [25] V.M. Garcia, M.T.S. Nair and P.K. Nair, "Optical properties of $PbSCu_xS$ and $Bi_2S_3Cu_xS$ thin films with reference to solar control and solar absorber applications," *Sol. Energy Mater.*, vol. 23, pp. 47-59, Nov. 1991.
- [26] Y.Y. Xi, T.L.Y. Cheung and D.H.L. Ng, "Synthesis of ternary $Zn_xCd_{1-x}S$ nanowires by thermal evaporation and the study of their photoluminescence," *Mater. Lett.* Vol. 62, pp. 128-132, 2008.
- [27] J.H. Lee, W.C. Song, J.S. Yi, K.J. Yang, W.D. Han and J. Hwang, "Growth and properties of the $Cd_{1-x}Zn_xS$ thin films for solar cell applications," *Thin Solid Films*, Vol. 431, pp. 349-353, 2003.
- [28] M.E. Rincon, M.W. Martinez and M. Miranda-Hernandez, *Sol. Energy Mater. Sol. Cells*, "Structural, optical and photoelectrochemical properties of screen-printed and sintered $(CdS)_x(ZnS)_{1-x}$ ($0 < x < 1$) films", vol. 77, pp. 25-40, 2003.
- [29] S.K. Deskmukh, A.V. Kokate and D.J. Sathe, "Thermal conductivity of $BaWO_4$ single crystal", *Mater. Sci. Eng.*, Vol. B 122, pp. 206, 2005.
- [30] X. J. Wu, D. Z. Shen, Z. Z. Zhang, J. Y. Zhang, K. W. Liu, B. H. Li, Y. M. Lu, D. X. Zhao, and B. Yao, "*p*-type conductivity and donor-acceptor pair emission in $Cd_{1-x}Fe_xS$ dilute magnetic semiconductors," *Appl. Phys. Lett.* Vol. 89, pp. 262118, 2006.
- [31] N. Badera, B. Godbole, S.B. Srivastava, P.N. Vishwakarma, and L.S. Sharath, "Quenching of photoconductivity in Fe doped CdS thin films prepared by spray pyrolysis technique", *Appl. Surf. Sci.*, vol. 254, pp. 7042-7048, 2008.
- [32] K.W. Liu, J.Y. Zhang, D.Z. Shen, B.H. Li, X.J. Wu, B.S. Li, Y.M. Lu and X.W. Fan, *Thin Solid Films*, "Growth optical and magnetic properties of $Cd_{1-x}Fe_xS$ films prepared on Al_2O_3 (0001), Vol. 515, pp. 8017-8021, 2007.
- [33] Elena Rabinovich, Ellen Wachtel and Gary Hodes, "Chemical bath deposition of single-phase $(Pb,Cd)S$ solid solutions", *Thin Solid Films*, vol. 517, pp. 737, 2008.
- [34] O. Kijatkina, M. Krunks, A. Mere, B. Mahrov and L. Dloczik,

- "CuInS₂ sprayed films on different metal oxide underlayers", Thin Solid Films, vol. 431-432, pp. 105-109, 2003.
- [35] M. Ali Yildirim, Aytunç Ates and Aykut Astam, "Annealing and light effect on structural, optical and electrical properties of CuS, CuZnS and ZnS thin films grown by the SILAR method," Physica E: Low-dimensional Systems and Nanostructures, vol. 41(8), pp. 1365-1372, Aug. 2009.
- [36] S.M. Pawar, A.V. Moholkar, K.Y. Rajpure, J.H. Kim, C.D. Lokhande and C.H. Bhosale, "Fabrication of Fe: CdSe solar rechargeable (semiconductor-septum) storage cells," Current Applied Physics, vol. 9, pp. 1122, 2009.
- [37] Y.Y. Xi, Teresa L.Y. Cheung, Dickon H.L. Ng, "Synthesis of ternary Zn_xCd_{1-x}S nanowires by thermal evaporation and the study of their photoluminescence," Materials Letters, vol. 62(1), pp. 128-132, Jan. 2008.
- [38] Alessandro Martucci, Jochen Fick, Serge-Émile LeBlanc, Michael LoCascio, Alain Hach, "Optical properties of PbS quantum dot doped sol-gel films," Journal of Non-Crystalline Solids, vol. 345-346, pp.639-642, Oct. 2004.
- [39] A. U. Ubale and V. P. Deshpande, "Effect of manganese inclusion on structural, optical and electrical properties of ZnO thin films," J. Alloys Comp., vol.500, pp.138-143, 2010.
- [40] A. U. Ubale and D.K. Kulkarni, "Effect of manganese inclusion on structural, optical and electrical properties of ZnO thin films," Ind. J. Pure Appl. Phy. Vol. 44, pp. 254 -259, 2006.
- [41] A. U. Ubale, "Effect of complexing agent on growth process and properties of nanostructured Bi₂S₃ thin films deposited by chemical bath deposition method," Mater. Chem. Phy. Vol. 121, pp.555-560, 2010.