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Influence of acetic acid complex on physical properties of spray deposited FeSe thin films

A. U. Ubale*, Y. S. Sakhare

Nanostructured Thin Film Materials Laboratory, Department of Physics,Govt. Vidarbha Institute of Science and Humanities, Amravati, India

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ABSTRACT

The iron selenide thin films were successfully deposited on to the glass substrates at 573 K temperature using spray pyrolysis technique. Along with Fe and Se source, acetic acid (CH_3-COOH) was used as a complexing agent during the deposition process. The structural, morphological, electrical and optical properties of the deposited films have been studied using X-ray diffraction, scanning electron microscopy, atomic force microscopy and UV-Vis spectrophotometer respectively. The XRD analysis shows that the spray deposited FeSe thin films are nano-crystalline with tetragonal lattice. The surface studies of FeSe films shows porous morphology with spherical grains which is improved with addition of acetic acid. The AFM image indicates that the as deposited FeSe thin films are uniform, compact and well covered to the substrate. The absorption studies shows that films have direct band gap which varies between 3.05 to 2.60 eV depending on the quality of acetic acid added in the spray solution. The variation of electrical resistivity with temperature confirms semiconductor behavior of FeSe.

***Keywords*:** Chalcogenides, Spray pyrolysis, SEM, AFM, Electrical and Optical properties.

INTRODUCTION

The nanocrystalline materials have opened an innovative phase in the field of electronic applications, since material properties could be changed by changing the crystallite size and/or thickness of the film. The transition metal chalcogenides represent an significant family of materials useful in various devices such as solar cells [1–6] superconductors [7, 8], sensors [9] and various in spintronicsdevices [10–12]. Iron selenide is an important compound from this group which is usually prepared by several techniques viz. sulphuration of iron predeposited films [13], selenization of evaporated iron thin films [14],low-pressure metal organic chemical vapor deposition (LP-MOCVD) [15], mechano-synthesis [16], selenization technique [17], molecular beam epitaxy [18], milling pure elemental powder of iron and selenium [19] and selenization of amorphous iron oxide thin films prepared by spray pyrolysis [20, 21]. Chen at al [22] have prepared FeSe thin films with tetragonal structure by electrochemical deposition method. The deposition mechanism was inferred that the Se^{4+} ions are reduced to Se and successively oxidized to Se^{2-}, which forms tetragonal FeSe with Fe^{2+}. Chen et al [23] have reported growth of epitaxial tetragonal iron selenide thin films on single crystal $SrTiO_3$ (001) and MgO (001) substrates by pulsed laser deposition method. The deposition temperature and annealing temperature are found critical for getting tetragonal phase of FeSe .The synthesis of nanocrystalline metal chalcogenide thin films by spray pyrolysis techniques is currently attracting considerable attention as it is comparatively inexpensive, simple and convenient for large area deposition. The aim of the present work is to develop spray pyrolysis method for the preparation of nanocrystalline FeSe thin films. The

work is concentrated mainly on the study of influence of acetic acid complex on the structural, electrical and optical properties of FeSe thin films.

MATERIALS AND METHODS

2. Experimental

FeSe thin films were deposited onto glass substrates using spray pyrolysis technique at 573 K temperature. During deposition theother preparative parameters especially spray rate (5ml/min), nozzle to substrate distance (25cm) etc were kept constant. In the deposition mechanism the nature of the substrate surface is very important in order to grow uniform film over the entire substrate surface. Extreme cleaning of the substrate is required, since the contaminated substrate surface provides nucleation sites facilitating the growth which results in non-uniform film growth. Hence cleaning of the substrate prior to the actual deposition is important. Commercially available glass micro slides of dimensions 26 mm×76 mm×2 mm were boiled in chromic acid for 30 min, then washed with liquid detergent and rinsed in acetone. Finally slides were ultrasonically cleaned with double distilled water for 15 min prior to the actual deposition. The SeO_2 solution was prepared by dissolving 1g of selenium powder (99% purity, Merck) with 10 ml nitric acid (HNO_3). It was then boiled for few minutes to get white residual powder inside the beaker. To it 100 ml of distilled water was added to prepare 0.13 M SeO_2 solution. To prepare spray solution 20 ml of 0.12 M Fe $(NO_3)_3.9H_2O$, 10 ml of CH_3-COOH and 20 ml of freshly prepared SeO_2 were mixed in a 100 ml beaker. In order to study the effect of complex CH_3-COOH, its volume in spray solution was changed from 0 to 20 ml (table 1).The thickness of the prepared film was measured by weight difference method, by considering the bulk density of iron selenide.The structural characterization of iron selenide thin films were carried out by analyzing the X-ray diffraction patterns obtained via a PANalyticalX'Pert PRO MRD X-ray diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) data were acquired from a JOEL'S JSM-7600F microscope having resolution of 1 nm. Atomic force micrographs (AFM) were collected using Park Scientific Instrument. The optical absorption studies were carried out using JASCO V-530 UV/Visible spectrophotometer at normal incidence, in the wavelength range 350-850 nm. To study the electrical characterization of the films, the dark electrical resistivity measurements were carried out using two point d.c. probe method in the temperature range 300-500K.The thermo-emf voltage developed across the film was measured to find the type of conductivity of FeSe.

Table1: Process parameters for the deposition of FeSe thin films

Spray Parameters	Optimum Value
Nozzle	Glass
Nozzle-substrate distance	25 cm
Ferric nitric	0.12 M
SeO_2	0.13 M
CH_3-COOH	0.12 M
Solvent	Distilled water
Solution flow rate	5ml /min
Carrier gas	Compress air
Substrate temperature	473 to 673 K

RESULTS AND DISCUSSION

3.1 Film formation mechanism

In spray pyrolysis method, the starting material is required to be in the solution form which, when sprayed onto the hot substrate, results in the formation of a thin film on it. The sprayed droplets undergo evaporation, thermal decomposition and condensation to produce well adherent FeSe thin films. The $Fe(NO_3)_3.9H_2O$ forms complex with acetic acid as $[Fe\ (CH_3COO)_6]^{3-}$ which then decomposes on hot substrate to produce FeSe. The mechanism of FeSe film deposition is essentially based on the complex iron acetate formed in the spray solution. The FeSe thin films deposited from un-complexed spray solution have thickness of the order of 82 nm which increases with acetic acid.In the absence of acetic acid Fe^{2+} ions vigorously reacts with Se^{2-} ions to give FeSe. The addition of acetic acid forms iron acetate which decomposes at hot substrate to produce FeSe. The FeSe film thickness increases with acetic acid (fig.1) and becomes 217 nm at 15 ml of acetic acid. Further addition of acetic acid decreases film thickness slightly.

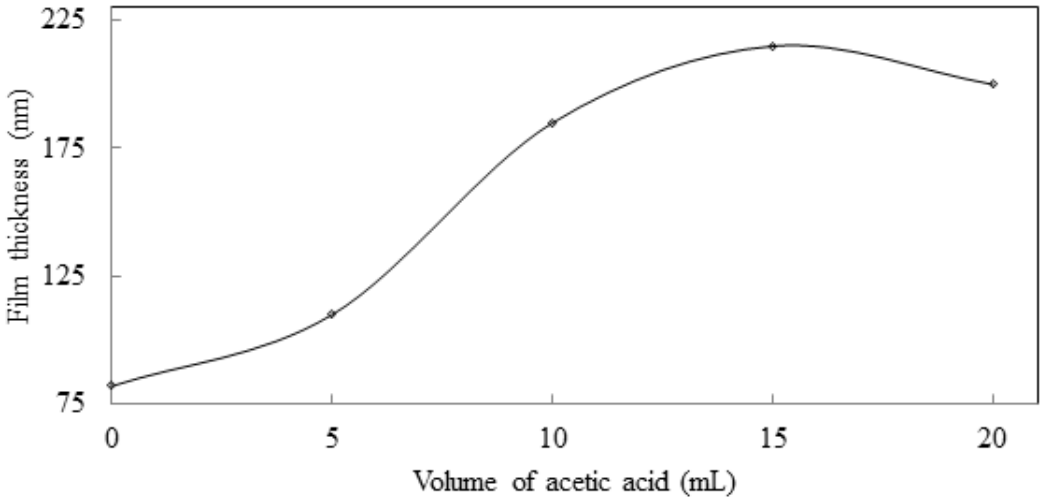

Fig.1 Variation of FeSe film thickness (nm) with volume of complexing agent (CH_3-COOH): (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

3.2 Structural Study

The X-ray diffraction (XRD) studies were carried out in order to determine the crystalline nature of the deposited films. The XRD patterns of spray deposited FeSe thin films deposited by changing acetic acid complex is shown in Fig.2. The inter-planar spacing'd' was calculated using the relation,

$D_{hkl}= (\lambda/2\sin\theta)$ (5)

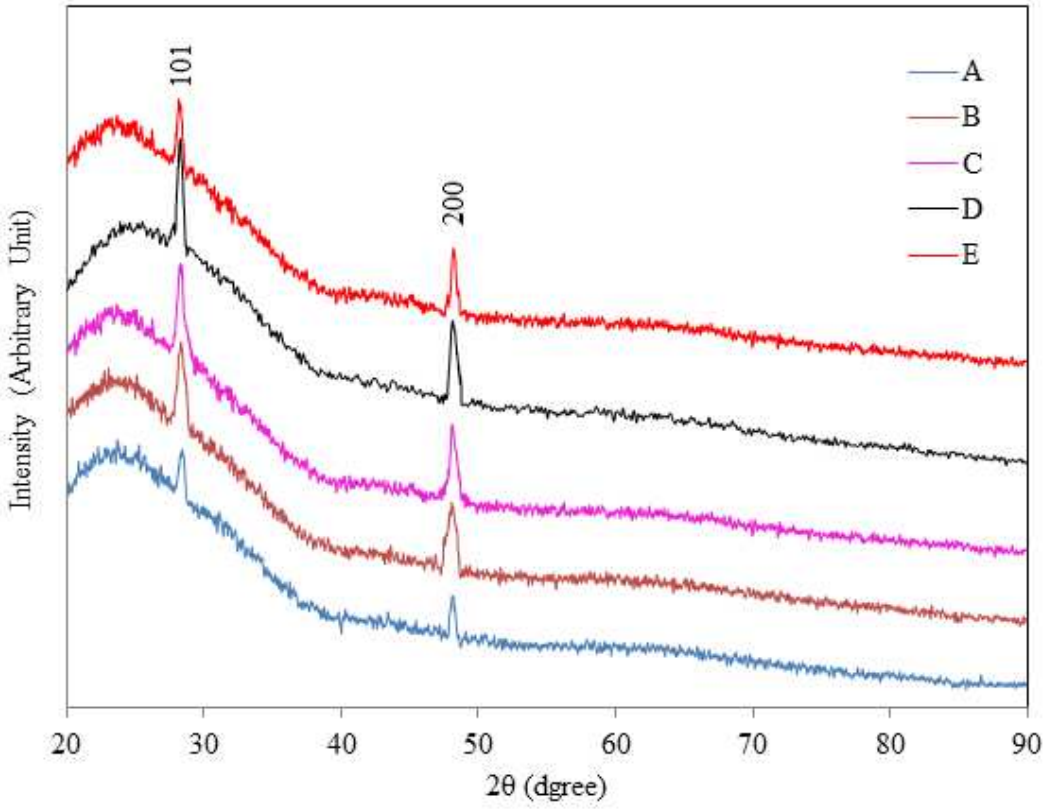

Fig.2. X-ray diffraction pattern of FeSe thin films deposited by changing the volume of complexing agent (CH_3-COOH) in spray solution: (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

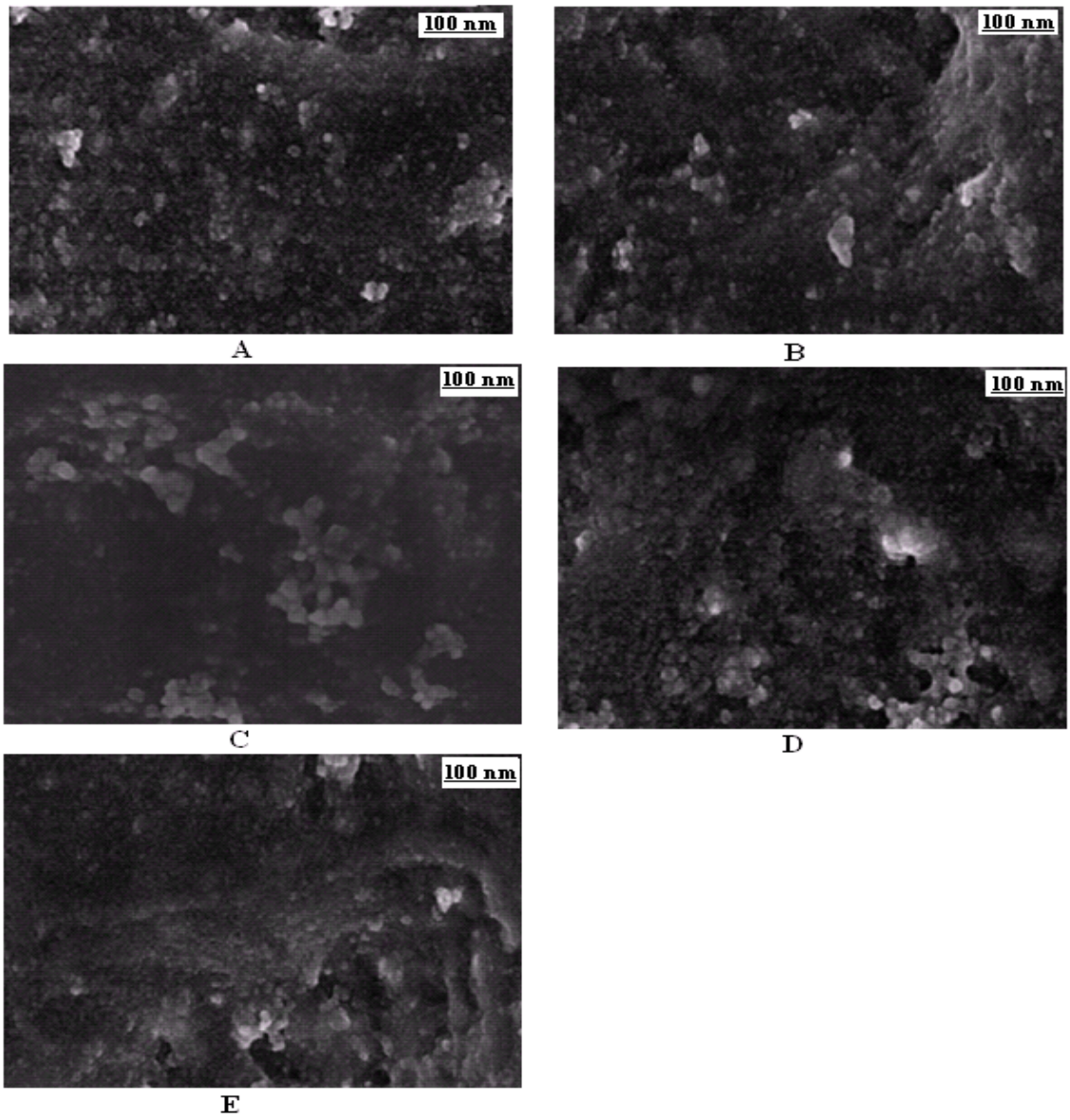

Fig.3. SEM images of FeSe thin films deposited by changing volume of complexing agent in spray solution: (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

It is observed that FeSe thin films are nanocrystalline in nature with tetragonal crystal structure. The observed'd' values are found to be in good agreement with the standard JCPDS data (Table 2). The diffraction peaks found around 2θ values of 28.681 and 48.308 degree are due to (101) and (200) lattice planes of tetragonal FeSe. The broad hump observed in the XRD pattern is due to amorphous glass substrate. As the film thickness increases the crystalline nature of the film is improved. The average crystallite size of the deposited material is determined by using Debye-Scherer's formula,

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

Where β is full width at half maximum of the peak in radians, λ is the wavelength of CuKα radiation (λ=1.5418 A^0), θ is the Bragg diffraction angle at peak position in degrees. The crystallite size of FeSe film deposited from un-complexed bath is 82 nm and it increases with addition of acetic acid complex in spray solution.

Table: 2 Comparison of observed and standard XRD data of FeSethin films(JCPDS Card : 85-0735)

Film thickness (nm)	Standard		Observed		Reflection plane (hkl)
	2θ	d	2θ	d	
82	28.681	3.110	28.220	3.112	101
	48.308	1.882	48.229	1.861	200
110	28.681	3.110	28.320	3.120	101
	48.308	1.882	48.229	1.863	200
185	28.681	3.110	28.420	3.112	101
	48.308	1.882	48.226	1.881	200
217	28.681	3.110	28.320	3.116	101
	48.308	1.882	48.236	1.891	200
200	28.681	3.110	28.320	3.111	101
	48.308	1.882	48.296	1.871	200

3.3 Morphological Properties

The surface morphology of the spray deposited FeSe thin film was investigated by scanning electron micrographs. Fig.3 Shows the SEM images of FeSe thin film on glass substrate deposited from un-complexed and complexed spray solution.

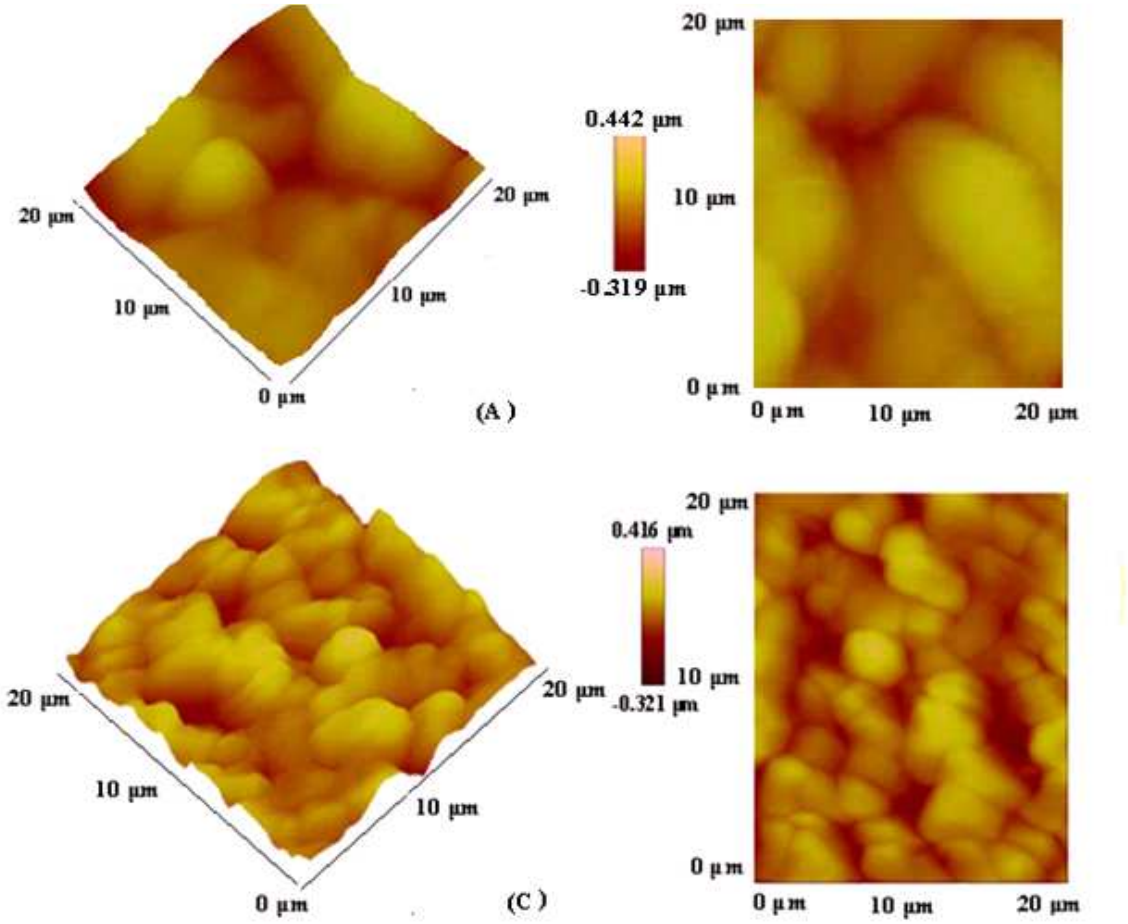

Fig.4. AFM image of FeSe thin film of thickness (A) 82 nm and (C) 185 nm.

From SEM, it is observed that FeSe thin films are uniform and pinhole free with randomly oriented spherical shaped grains covering the substrate. The spherical grains are uniformly distributed over smooth homogenous background. The observed grain growth increases with acetic acid in spray solution.Three-dimensional surface morphology of the spray deposited FeSe thin films was investigated from atomic force micrographs. Fig. 4(A) and (C) shows the 3D and 2D AFM images of FeSe films deposited at 0 ml and 10 ml of acetic acid. It can be seen that spray deposited FeSe thin film have granular structure. In addition to granular nature, the film substrate is dense, uniform with no cracking or voids are observed.

3.4 Optical Properties

The absorption spectra of FeSe films deposited by changing quantity of acetic acid complex in spray solution is studied in the wavelength range 350–900 nm, without accounting reflection and transmission losses [Fig.5].

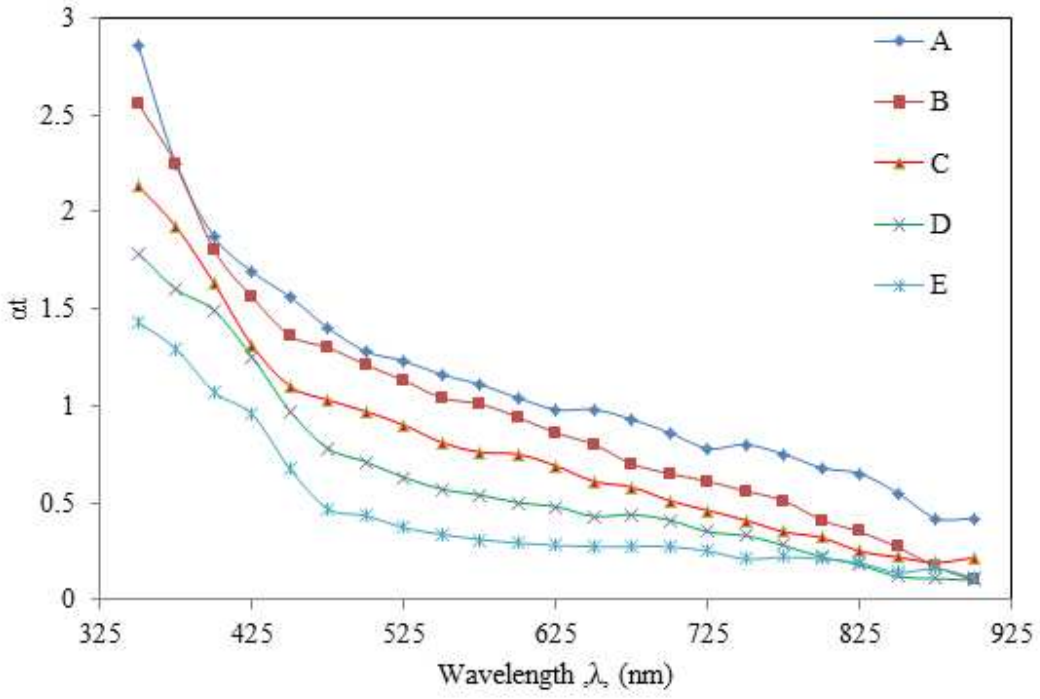

Fig.5. Plots of optical absorption (αt) versus wavelength (nm) for FeSe thin films deposited by changing volume of complexing agent (CH_3-COOH): (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

The absorption data were analyzed using the classical relation,

$$\alpha h\upsilon = A(Eg - h\upsilon)^n \qquad (8)$$

Where 'A' is a constant, 'Eg', is the band gap and 'n' is number equal to 1 for direct gap and 2for indirect gap semiconductors.The plot of $(\alpha h\upsilon)^2$ versus hυ has linear nature (Fig.6),indicating the mode of transition in these films is of direct type. The Extrapolation of the linear portion of the curve on energy axis at zero absorption coefficient, gives the value of optical band gap energy.

The optical band gap of FeSe film deposited from un-complexed spray solution was found to be 3.05eV which is quite low as compared to the earlier report of by Luo and Furdyna [24].The decrease in band gap from 3.05 to 2.60 is observed with addition of acetic acid in spray solution from 0 to 20 ml [fig.7].

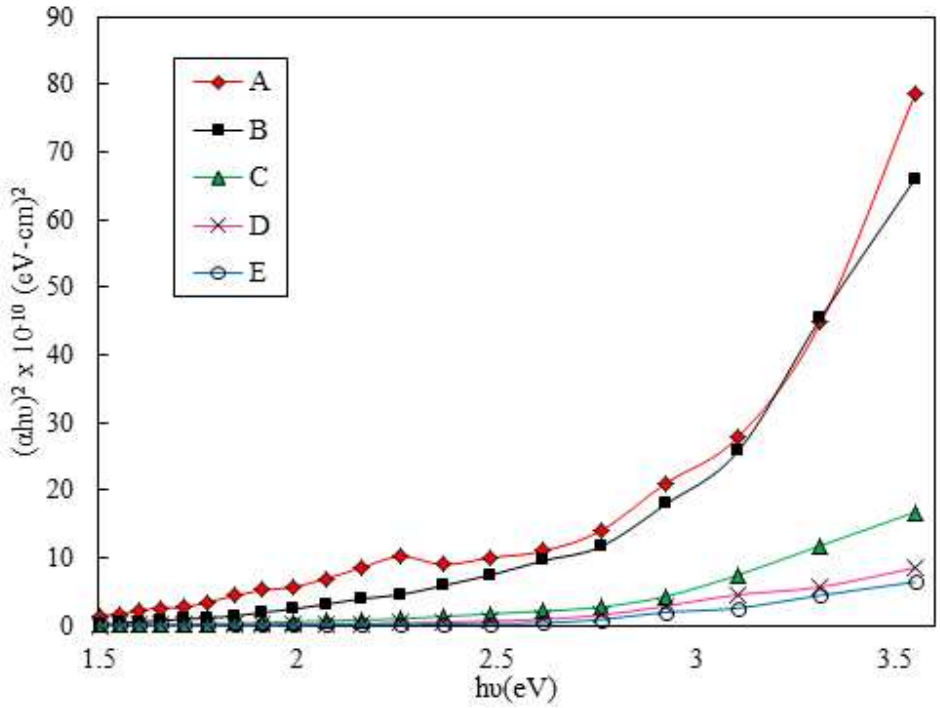

Fig.6. Plots of $(\alpha h\upsilon)^2$ versus hυ for FeSe films deposited by changing volume of complexing agent (CH_3-COOH): (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

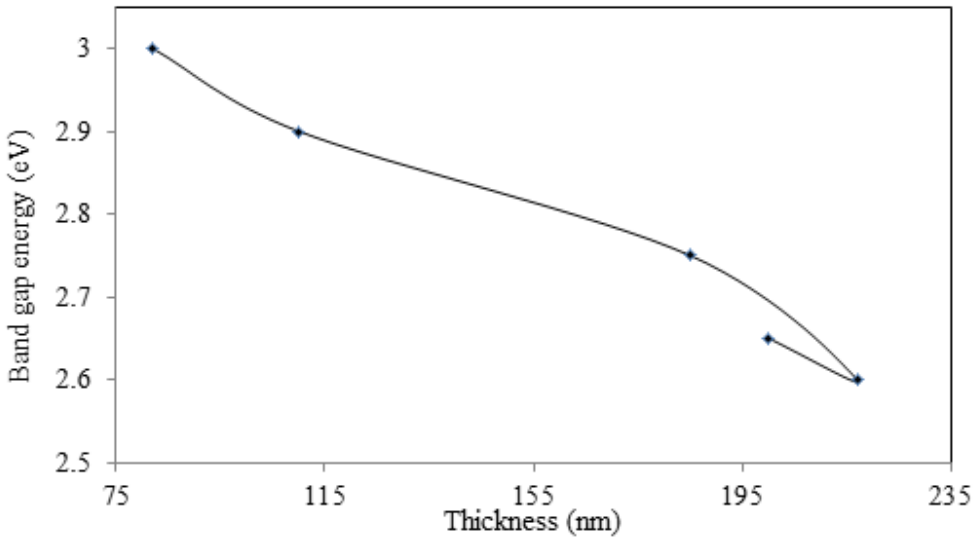

Fig.7. Variation Optical band gap energy (eV) of FeSe thinfilm with volume of complexing agent (CH_3-COOH): (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

3.5 Electrical Properties

The two-point dc probe method of dark electrical resistivity measurement was used to study the variation of electrical resistivity with temperature. The room temperature electrical resistivity of FeSe film deposited without complex was found to be of the order of 6 x 10^3 Ω cm. This resistivity decreases with addition of acetic acid in spray solution [fig.8]. It may be due to improvement in crystalline nature of FeSe with acetic acid. The high value of resistivity may be attributed due to nanocrystallinity of film, grain boundary discontinuities, presence of surface states, small thickness of the film, etc. The variation of log ρ with reciprocal of temperature (K^{-1}) is depicted in Fig.9.The activation energies were calculated using the relation.

$$\rho = \rho_o\left(\frac{E_a}{KT}\right) \qquad (9)$$

Where ρ is the resistivity at temperature T, ρ_o is a constant (room temperature resistivity), K is the Boltzmann's constant and T is the absolute temperature respectively.The activation energy represents the location of trap levels below the conduction band. The spray deposited FeSe thin films shows two distinct activation energy regimes. This clearly indicates that different scattering mechanisms are operative in the two regimes. The activation energy in low temperature regime and high temperature regime is 0.15 and 1.04 eV for FeSe film deposited without acetic acid and it decreases to 0.12 and 0.77 eV respectively [fig.10](Table3). The activation energies are mainly influenced by native defects such as iron interstitials and selenide vacancies, which cause to increase the donor levels below the Fermi level.

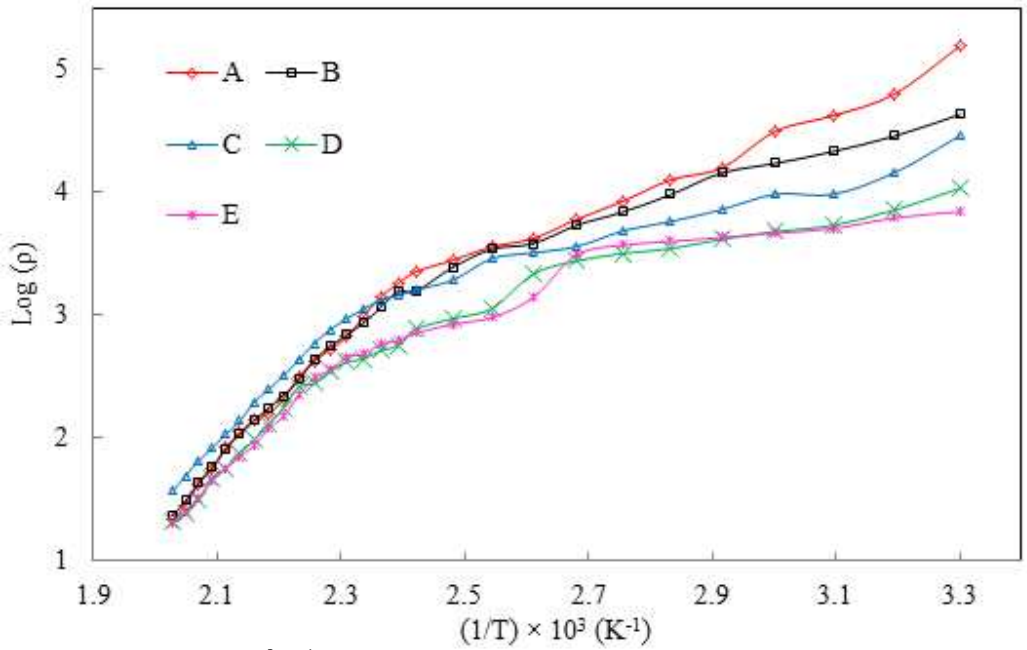

Fig.8. Variation of log (ρ) vs 1/T x 10^3 (K^{-1}) for FeSe films deposited by changing volume of complexing agent (CH_3-COOH) in spray solution: (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

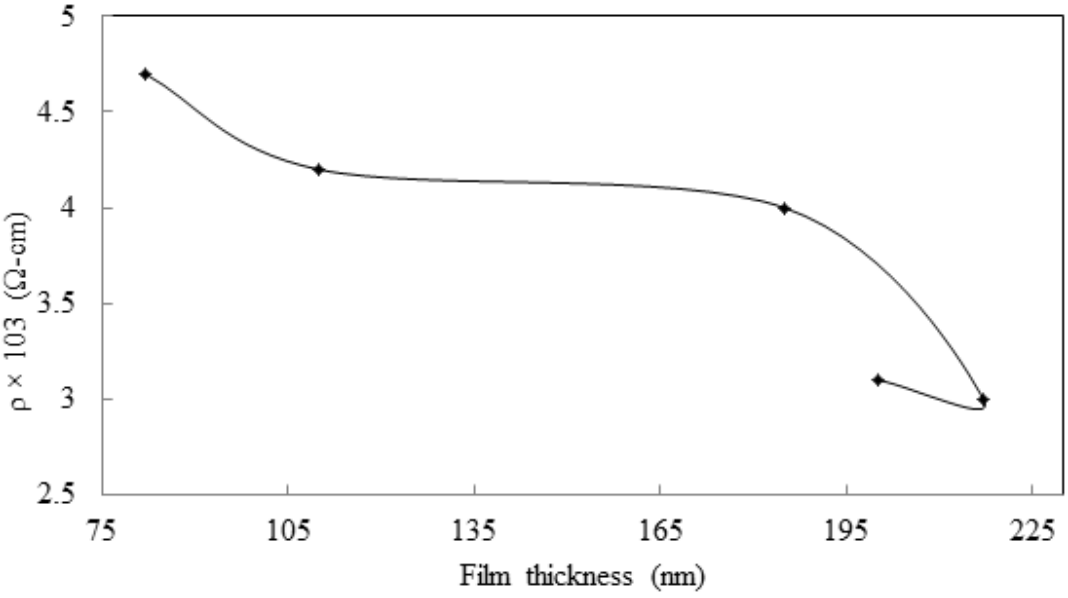

Fig.9.Variation of electrical resistivity (Ω-cm) of FeSe at 373 K temperature with film thickness (nm).

Table3: Grain size, Electrical resistivity at 373 K, band gap energy and activation energy of FeSe thin films

Sample	Volume of Acetic Acid (ml)	Thickness (nm)	Band Gap Energy (eV)	Activation Energy (eV)		Grain size(nm)	ρ 10^4(Ω-cm)
				Low Temperature region	High Temperature region		
A	00	082	3.05	0.15	1.04	17	6
B	05	110	2.90	0.15	1.0	28	5.3
C	10	185	2.75	0.14	0.83	40	4
D	15	217	2.60	0.11	0.76	53	1.5
E	20	200	2.65	0.12	0.77	51	3.2

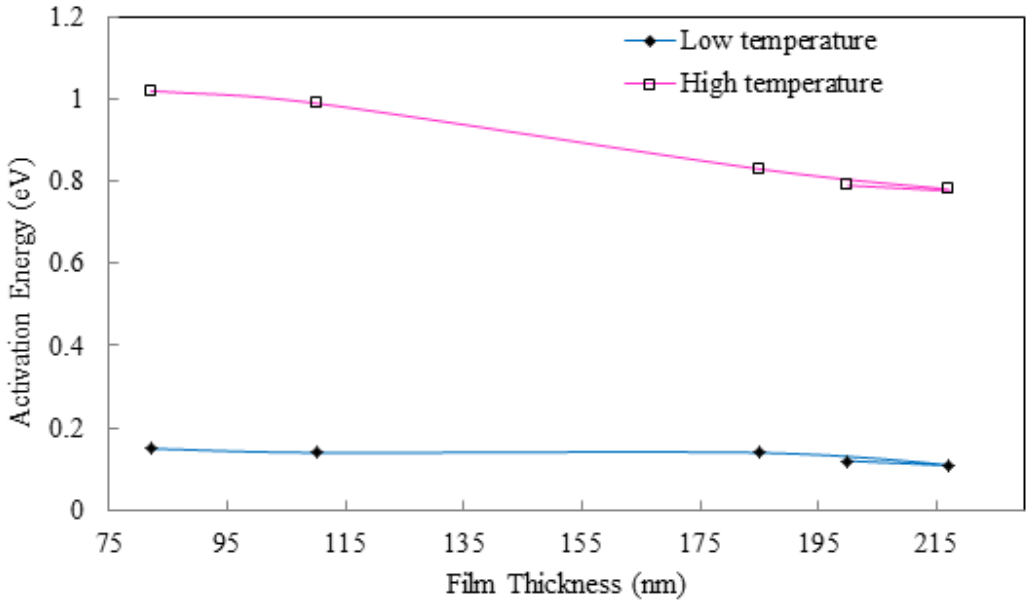

Fig.10. Variation of activation energy (eV) of FeSe filmwith film thickness (nm).

3.6 Thermo-emf measurement

The temperature difference applied across the length of the film causes the transport of carriers from the hot end to the cold end and thus creates an electric field, which gives the thermal voltage. This thermally generated voltage is directly proportional to the temperature difference applied across the semiconductor. The polarity of the induced emf for FeSe film deposited from complexed and un-complexed spray solution indicates p-type electrical conductivity [Fig.11], which is in good agreement with earlier reports by S.M.Pawar et al. [25]. It is also observed that the thermo-emf developed across the film is found thickness dependent

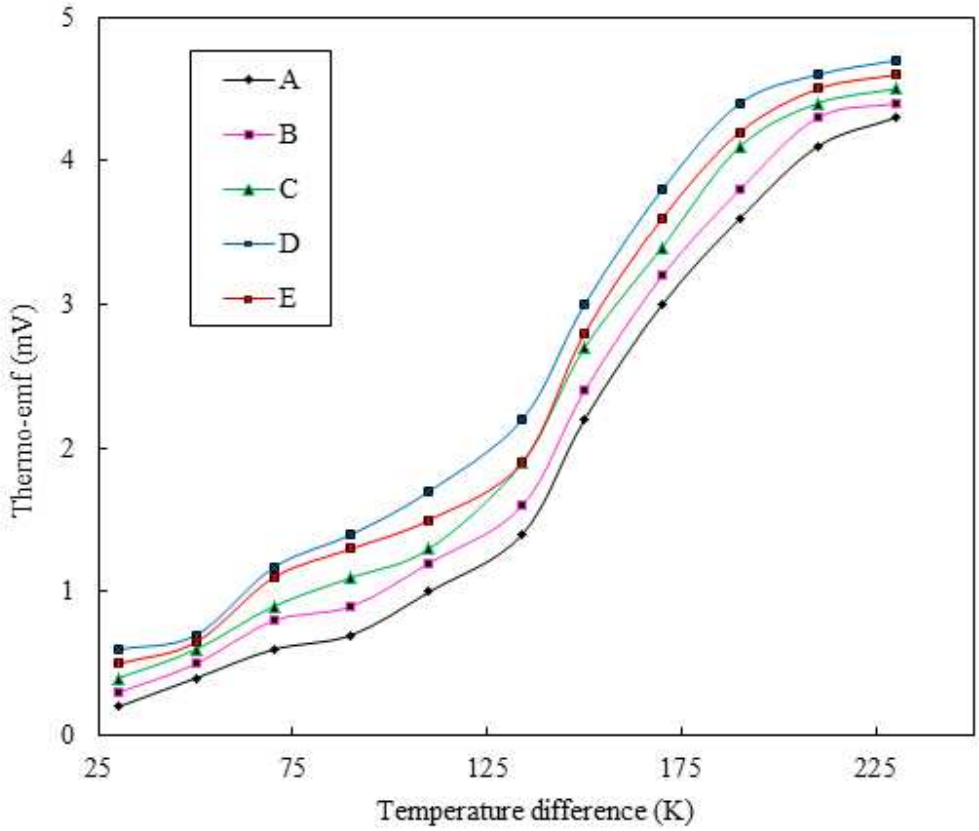

Fig: 11.Variation of thermo-emf (mV) versus temperature differences for the FeSe thin films deposited by changing volume of complexing agent (CH_3-COOH) in spray solution: (A) 0ml, (B) 5 ml, (C) 10ml, (D) 15ml and (E) 20 ml.

CONCLUSIONS

In conclusion, iron selenide thin films were successfully prepared from acetic acid complexed and un-complexed spray solution using spray pyrolysis technique. The XRD studies revealed that the spray deposited FeSe thin films are tetragonalin nature. The SEM analysis shows that the FeSe thin films are uniform, homogenous and well covered to the substrate. The AFM images of FeSe films show granular structure.The optical absorption studies show that the FeSe films deposited from un-complexed bath has optical direct bandgap 3.05eV and it decreases with addition of acetic acid in spray solution. The electrical resistivity of FeSe film at room temperature was found to be of the order of 6 x $10^3\Omega$ cm and it decreases with acetic acid.

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