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Optical properties of FeSe thin films deposited by chemicalbath deposition technique: Effect of molar concentration of Fe $(NO_3)_3.9H_2O$

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ABSTRACT

Chemical bath deposition (CBD) technique is very attractive, since it is relatively simple, economic and convenient to grow nanostructured chalcogenide thin films at room temperature. In this paper the effect of Fe ion source, Fe $(NO_3)_3.9H_20$ *on optical properties of FeSe thin films is discussed.The as deposited FeSe thin films are polycrystalline in nature with tetragonal lattice. The optical absorption measurements show that the optical band gap energy of FeSe changes from 2.67 to 2.60 eV depending on Fe ion concentration in deposition bath.*

Keywords: Chalcogenides, Chemical synthesis, XRD and Optical properties.

INTRODUCTION

Investigations on nanostructured chalcogenide thin films are constantly under progress to develop new potential materials suitable for solar energy conversion devices. The transition metal chalcogenides represent a significant family of materials useful in various devices such as superconductors [1, 2], sensors [3], solar cells [4–9] and various spintronicsdevices [10–12]. Iron selenide is an important compound from this group which is usually prepared by several techniques viz. low-pressure metal organic chemical vapor deposition [13], molecular beam epitaxy [14], milling pure elemental powder of iron and selenium [15], mechano-synthesis [16], selenization technique [17], sulphuration of iron predeposited films [18], selenization of evaporated iron thin films [19] and selenization of amorphous iron oxide thin films prepared by spray pyrolysis [20, 21].Ubale et al [22] have prepared FeSe thin films with tetragonal structure by chemical bath deposition method.Recently there has been considerable interest in energy conversion devices fabricated from nanocrystalline thin films deposited using low cost chemical techniques such as chemical bath deposition, sol gel, successive ionic layer adsorption and reaction, electrodeposition and spray pyrolysis. Out of these chemical methods, chemical bath deposition method has found out a special attention as it is least expensive, low temperature method and non-pollutant. In CBD the semiconductor thin films are deposited on substrates immersed in dilute solutions containing metal ions along with sulfide or selenide ions.This offers minimum toxicity and occupational hazards. Even though many reports are available on chalcogenide and selenide thin films by CBD, but very few reportsare available for FeSe thin films [22]. The objective of the present study is to prepareFeSe thin films on glass substrates by chemical bath deposition technique and investigate the effect of Fe ion source on its optical properties.

MATERIALS AND METHODS

In CBD deposition process the controlled precipitation of a compound from the solution on a suitable substrate is involved. This method offers many advantages over other more established physical methods. The deposition parameters such as, deposition time, pH of bath, reagent concentrations, etc. are easily adjusted to get good quality nanostructured thin films. Thin films of iron selenide were grown by using slow release of Fe^{2+} ions from EDTA complexed Fe salt and Se^{2-} ions in aqueous medium using CBD method. The analytical grade reagents $Fe(NO_3)_3.9H_20$, EDTA and Se metals powder and sodium sulfide were used in the present work. The Na_2SeSO_3 solution was prepared by mixing 10 g of selenium powder (99% purity, Merck) with 100 g anhydrous sodium sulfite in 500 ml of distilled water with constant stirring for 10 h at 80^0C. It was then sealed and kept overnight, since on cooling, a little selenium separated out from the solution. Finally, it was filtered to obtain a clear solutionof Na_2SeSO_3 of 0.13 M. The commercially available glass micro slides of dimensions 26 mm×76 mm×2 mm were boiled in chromic acid for 30 min and were washed with double distilled water. The substrates were then washed with liquid detergent and rinsed in acetone. Finally slides were ultrasonically cleaned for 15 minin double distilled water prior to the actual deposition. For the deposition of FeSe thin films 40 ml of 0.03 M, Fe $(NO_3)_3.9H_2O$ was mixed with 20 ml of 0.1M, EDTA and 40 ml of freshly prepared 0.13 M, Na_2SeSO_3.The uniform and well adherent and reflecting orange brown coloured thin films were removed after 72 h deposition time from the bath and washed with distilled water.In order to investigate the effect of molar concentration of Fe $(NO_3)_3.9H_2O$ on the structural and optical properties, six different sets of FeSe films were prepared by changing its molar concentration from 0.03 to 0.18 M(Table 1). With the help of sensitive microbalance the FeSe film thickness was measured by gravimetric method using the relation,

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

Where m is the mass of the deposited film, A is area of film and ρ is bulk density of FeSe. The X-ray diffraction (XRD) studies were carried by usingPANalyticalX'Pert PRO MRD X-ray diffractometer with CuKα radiation in the two theta range from 20 to 90 degree. The optical absorption studieswere carried out with a JASCO V-530 UV/Visible spectrophotometer system at normal incidence in the wavelength range 300 to 900 nm.

RESULTS AND DISCUSSION

3.1 Film formation mechanism

The deposition of FeSe thin film occurs when the ionic product of Fe^{2+} and Se^{2-}ions exceeds the solubility product of FeSe. The controlled release of Fe^{2+} and Se^{2-}ions in the solution controls the rate of precipitation and hence the rate of film formation. The steps involved in the chemical deposition of FeSe thin films are given below.

The hydrolysis of sodium selenosulphate (Na_2SeSO_3) takes place to give Se^{2-}ions as,

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^- \qquad (2)$$

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-} \qquad (3)$$

The metal ions from $Fe(NO_3)_3.9H_20$ forms complex with EDTA as,

$$Fe(NO_3)_3.9H_2O + EDTA_{(aq)} \rightarrow [FeEDTA]^{2+} + (NO_3)^- \qquad (4)$$

The complex decomposition takes place to release Fe^{2+} ions,

$$[FeEDTA]^{2+} \rightarrow Fe^{2+} + EDTA_{(aq)} \qquad (5)$$

Finally, FeSe thin film formation takes place as,

$$Fe^{2+} + Se^{2-} \rightarrow FeSe \downarrow \qquad (6)$$

3.2 Structural Study

Figure 1 shows the XRD patterns of the FeSe thin films deposited at various molar concentrations of $Fe(N0_3)_3.9H_2O$. The observed XRD data of FeSe films are in good agreement with standard JCPDS data (JCPDS data card No.085-0735 and 71-2250, table1). The inter-planar spacing'd' was calculated using the relation [23],

$$D_{hkl} = (\lambda/2\ Sin\theta) \qquad (7)$$

Where λ is the wavelength used (0.154 nm) and θ is the Bragg's angle.

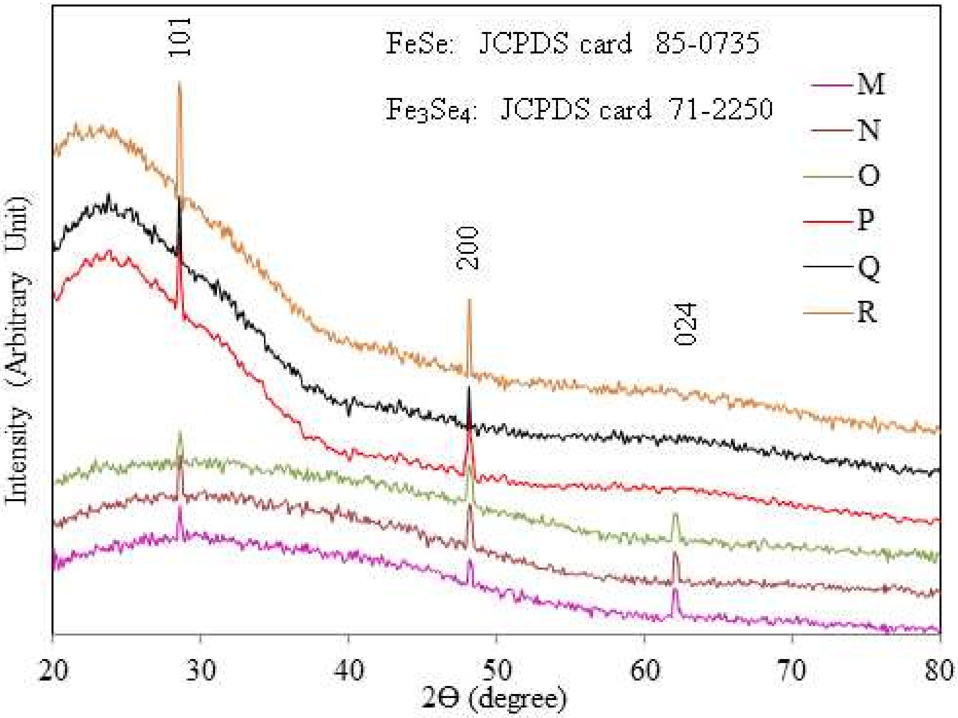

Fig.1. X-ray diffraction pattern of FeSe thin films deposited at various molar concentrations of $Fe(NO_3)_3.9H_2O$: (M) 0.03M ,(N) 0.06M , (O) 0.09M , (P) 0.12M ,(Q) 0.15M and (R) 0.18M.

Table: 1 Comparison of observed and standard XRD data of FeSethin films(JCPDS Card : 85-0735 and 71-2250).

Film	Concentration of $Fe(NO_3)_3.9H_2O$	Thickness (nm)	Standard		Observed		h k l	Phase
			2Θ (degree)	d (A^0)	2Θ (degree)	d (A^0)		
M	0.03 M	156	28.681	3.110	28.693	3.112	101	FeSe
			48.308	1.882	48.288	1.886	200	FeSe
			61.831	1.499	61.890	1.498	024	Fe_3Se_4
N	0.06 M	208	28.681	3.110	28.663	3.111	101	FeSe
			48.308	1.882	48.302	1.887	200	FeSe
			61.831	1.499	61.834	1.495	024	Fe_3Se_4
O	0.09 M	237	28.681	3.110	28.702	3.118	101	FeSe
			48.308	1.882	48.297	1.883	200	FeSe
			61.831	1.499	61.840	1.499	024	Fe_3Se_4
P	0.12 M	270	28.681	3.110	28.690	3.113	101	FeSe
			48.308	1.882	48.291	1.879	200	FeSe
Q	0.15 M	257	28.681	3.110	28.667	3.115	101	FeSe
			48.308	1.882	48.304	1.888	200	FeSe
R	0.18 M	240	28.681	3.110	28.645	3.118	101	FeSe
			48.308	1.882	48.310	1.886	200	FeSe

The CBD deposited FeSe films are nanocrystalline in nature with tetragonal lattice. The peaks observed around 28.681 and 48.308 corresponds to the (101) and (200) orientations due to tetragonal phase. However, the (230) orientation is observed at lower thickness due to monoclinic Fe_3Se_4. At lower molar concentration the numbers of Fe^{2+} ions available to from FeSe phase are less as compare to Se^{2-} ions.

The average crystallite size was determined from (101) and (200) diffraction peaks using the Scherrer formula [24],

$$d = \frac{0.9\,\lambda}{\beta \mathrm{Cos}\,\theta} \qquad (8)$$

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 grain size at 0.03 molar concentration is 45 nm and it increases to 81 nm at 0.12 molar concentration and then again decreases for further rise in concentration. The crystallite size has thus shown dependence on deposition mechanism, the cluster-by-cluster mechanism at higher concentration gives smaller grains than the ion-by-ion mechanism at lower concentration.

3.3 Optical Properties

The optical properties of FeSe thin films deposited by chemical bath deposition technique on glass substrate were investigated by measuring optical absorbance in the wavelength range 300 to 900 nm.The plots of optical absorbance (αt) versus wavelength (λ) of FeSe thin films are shown in Fig.2.

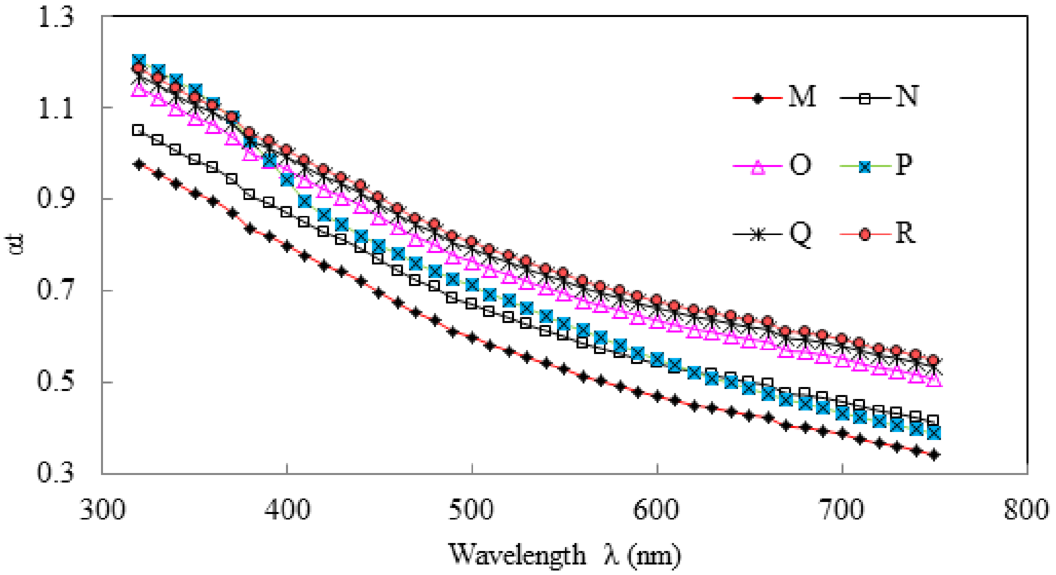

Fig.2. Plots of optical absorption (αt) versus wavelength (nm) of FeSe thin films deposited at various moler concentrations of $Fe(NO_3)_3.9H_2O$: (M) 0.03M ,(N) 0.06M , (O) 0.09M , (P) 0.12M ,(Q) 0.15M and (R) 0.18M.

In the spectra a quick inclining trend was observed, however not clear and sharp absorption edge can be determined, which is consistent with the amorphous or nanocrystalline structure of FeSe thin films. The absorption coefficient (α) and the photon energy (hυ) obeys the following equation[25-29],

$$\alpha h\upsilon = A(Eg - h\upsilon)^n \qquad (9)$$

Where 'A' is a constant, 'Eg' is the FeSe band gap and 'n' is a number equal to 1 for direct band gap and 2 for indirect band gap. Figure 3 shows the plots of $(\alpha h\upsilon)^2$ versus hυ for FeSe thin films.

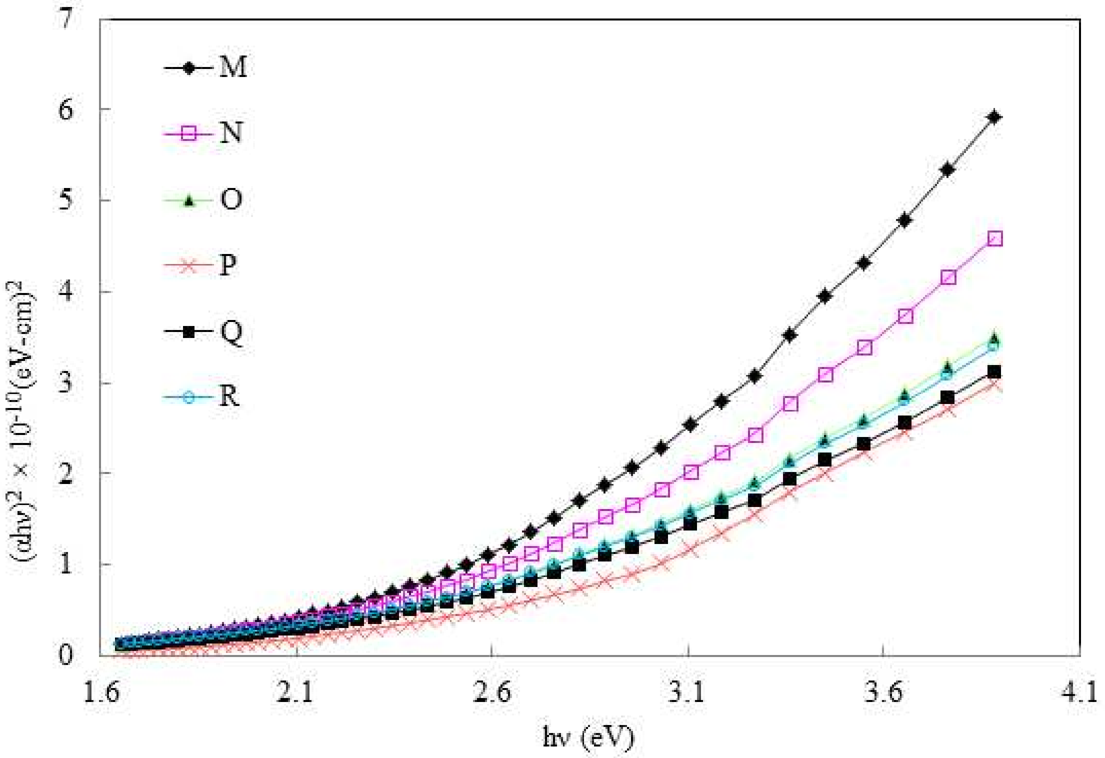

Fig.3. Plots of $(\alpha h\upsilon)^2$ versus hυ for FeSe thin films deposited at various molar concentrations of $Fe(NO_3)_3.9H_2O$: (M) 0.03M ,(N) 0.06M , (O) 0.09M , (P) 0.12M ,(Q) 0.15M and (R) 0.18M.

The band gap of FeSe film is estimated by extrapolating the straight portion of curve to hυ axis at α=0. It is observed that optical band gap of FeSe film was decreased from 2.67 to 2.60 eV as molar concentration of Fe is changed from 0.03 to 0.12 M (fig.4). Also it is seen that at higher molar concentration of Fe from i.e. 0.12 to 0.18 M the band gap increased to 2.64 eV. This change in optical band gap is due to improvement in crystalline nature with thickness. As compare to earlier reports the optical band gap of FeSe is quite more which may be due quantum confinement and different size effects that arises in nanostructured thin film.

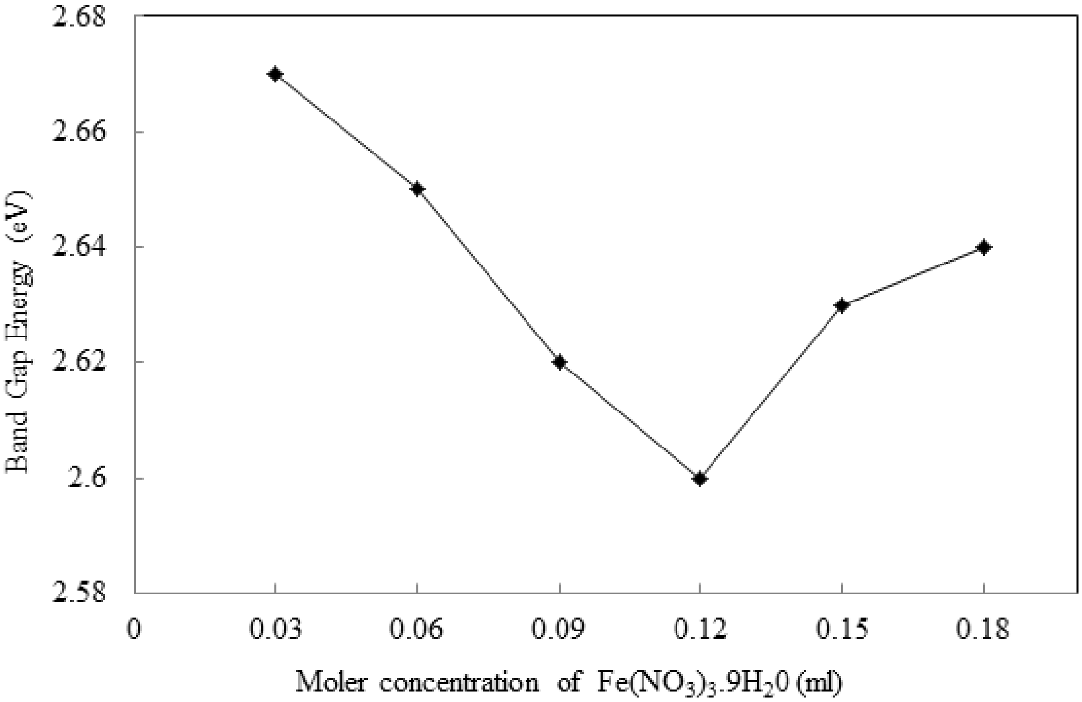

Fig.4. Variation optical band gap energy (eV) of FeSe with moler concentration of $Fe(NO_3)_3.9H_2O$: (M) 0.03M ,(N) 0.06M , (O) 0.09M , (P) 0.12M ,(Q) 0.15M and (R) 0.18M.

CONCLUSION

In conclusion, FeSe thin films with tetragonal crystal structure were deposited using chemical bath deposition method on to glass substrate. Optical studies showed that the band gap of FeSe is 2.67 at 0.03 molar concentration of $Fe(NO_3)_3.9H_20$ and it decreases to 2.60 eV at 0.12 molar concentration of Fe $(NO_3)_3.9H_2O$.

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