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Optical and Electrical Transport Properties of Transition Metal Dichalcogenide $MoSe_2$ Thin Films

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ABSTRACT

The transition metal dichalcogenide, $MoSe_2$ thin films were deposited on glass and stainless steel substrates by using Arrested Precipitation Technique. The reaction between MoO_3, TEA, Sodium dithionate and Sodium selenosulphate in an aqueous alkaline medium at 333 K has been used for synthesis. The deposited thin films have been characterized by using optical absorption, x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), atomic force microscopy (AFM),and electrical transport properties.The optical absorption study shows direct transition having band gap of 1.76 eV. The x-ray diffraction study reveals that the films are polycrystalline with hexagonal crystal structure. The electrical transport property studies revealed that the temperature dependence of an electrical conductivity has a distinct conduction region. The thermoelectric power measurements showed that the thermally generated voltage was of the order of several microvolts and exhibited n-type conduction. The surface morphology study by SEM and AFM shows that the grains are uniformly distributed over the entire surface and the deposition is uniform, compact and pin hole free.EDAX study reveals the stoichiometric nature of the films.

Keywords: Transition metal dichalcogenide, Thin films, Chemical Synthesis, Optical properties, Scanning Electron Microscopy, X-ray diffraction, Electrical transport properties.

INTRODUCTION

The Transition Metal Dichalcogenides of VI^B group elements are promising candidates for optoelectronic properties. The $MoSe_2$ is one of that, which is the important candidate for Photovoltaic conversion. The polycrystalline $MoSe_2$ thin films are effective photoelectrodes for Photoelectrochemical solar cells. These films are economically desirable for solar cells. The aim of the present investigation is to prepare the MoSe2 thin film and characterize it for its optostructural, morphological, compositional and electrical transport properties. It is important material because of its well matched band gap energy with the effective part of the solar spectrum.

Like MoS_2, $MoSe_2$ also resembles graphite in appearance and having excellent lubricating properties, hence it is used as a lubricant additive and as a solid lubricant however $MoSe_2$ is not found in nature. It is grey black compound with covalent character [1]. The VI^B-VI^A group metal dichalcogenides are crystalline with layered structure. Their single crystals attract the attention of researchers because of their potential electrochemical applications. However, only few experiments have been made on sputtered $MoSe_2$ films and these have dealt with the lubrication properties of the material [2, 3]. Krishana C. et al. have synthesized Semiconducting $MoSe_2$ thin film chemically and characterized by various Physical methods [4]. Among the various methods used for the preparation of metal chalcogenide thin films, the most convenient arrested precipitation technique was selected and employed for the preparation of $MoSe_2$ thin films in the present investigation. Because it has several advantages over the other methods such as low cost, low processing temperature, ability of large area deposition, control over the qualitative and quantitative nature of deposition [5]. In the present investigation, preparative parameters are optimized in order to obtain high-quality and well reproductive $MoSe_2$ thin films. The resulting films were uniform, adherent and a crack free and pin hole free thin films.

MATERIALS AND METHODS

Molybdenum *diselenide* thin films have been prepared by an arrested precipitation technique [6,7] by allowing the Mo-TEA complex to react with Se^{2-} ions, which are released slowly by the dissociation of Na_2SeSO_3 in alkaline medium at pH 9.6 Microscope glass slides of dimensions 75 mm x 25 mm x1.35 mm and fluorine doped tin oxide ($F:SnO_2$) coated glass slides as well as stain less steel plates were used as substrates. They were washed with detergent solution and then with double distilled water followed by boilling in chromic acid for 20 minutes and rinsed with double distilled water,at last cleaned with acetone and dried. Thoroughly cleaned glass substrates were mounted on a specially designed substrate holder. The deposition bath was prepared in 150 mL beaker by addition of 20 mL (0.25M) Mo-TEA complex,10 mL (10%)ammonium acetate 5 mL (2M) acetic acid,10ml sodium dithionate solution,and 20 mL (0.25M) solution of sodium selenosulphate the total volume of reaction mixture was made 100 ml adding double distilled water and final PH of the solution was made 9.6 by adding ammonia solution. The uniform well adherent reflecting black coloured thin films with terminal growth of thickness 900 nm have been deposited at 60^oC temperature and 50 rpm speed of substrate rotation in 55 minutes.

The principle of the thin film deposition is based on the slow release of $Mo^{4+}$and Se^{2-} ions by corresponding complexing agent and subsequent heterogeneous nucleation of $MoSe_2$ thin films on the ordinary glass substrate.

The optical absorption was carried out in the range of 350 to 850 nm with Hitachi-350 UV-Vis-NIR spectrophotometer.The absorption coefficient,band gap and type of transition were determined from these studies. The films were characterised for their structural properties by using a Bruker AXS Model D-8 advacne X-ray diffractometer for the 2θ ranging from 0^0 to 100^0 with CuKa line used as a beam (λ=1.5418 A^0), SEM pictures and energy dispersive X-ray analysis were recorded on JEAOL-JSM-6360-A, scanning microscope. The electrical transport properties of the film was studied by two point DC Probe method. The electrical conductivity and TEP measurement was carried out in the range of 300-500. The AFM studies were carried out by using JEAOL-JSM microscope to find the surface morphology of the resulting films.

RESULTS AND DISCUSSION

3.1 Growth Mechanism

Molybdenum diselenide thin films were deposited from an aqueous alkaline medium containing Mo-TEA complex and Se^{2-} ions.

The deposition process based on simple ion by ion mechanism it involves three steps
I) Dissociation of complex to free Mo^{4+} ions
ii) Formation of Se^{2-} ions
iii) $MoSe_2$ formation by ionic reaction
In this in the beginning, the Mo-TEA complex dissociates and release Mo^{4+} ions.

$$(NH_4)_2[Mo(N(CH_2—CH_2—O)_3)_2]+ 6H_2O \xrightarrow{pH9.6} Mo_4^{+} +2NH_4OH +2N\ (CH_2—CH_2—OH)_3)+4OH^{-}$$

Similarly the Sodium Selenosulphite hydrolyses and forms Se^{2-} ions. It followed by the formation of $MoSe_2$, it occurs by condensation on ion by ion basis on the glass substrate. The formation of $MoSe_2$ is possible when the ionic product of Mo^{4+} and S^{2-} ions exceeds the solubility product of $MoSe_2$. In the present investigation, the formation of $MoSe_2$ involves hydrolysis of sodium selenosulphite which releases the selenium ions in to the reaction bath. In an aqueous alkaline medium sodium selenosulphite hydrolysed to give Se^{2-} ions as

$$Na_2SeSO_3 + OH^- \leftrightarrow Na_2So_4 + HSe^-$$
$$HSe^- + OH^- \leftrightarrow Se^{2-} + H_2O$$

It is clear from these reactions that the equilibrium constant of HSe^- is predominant in the solution. The concentration of Se^- ions can be increased by addition of the excessive hydroxide ions to facilitate forward reaction[11]. The reaction 3.3 and 3.4 reveal that Mo^{4+} and Se^{2-} ions will condense ion by ion on the glass substrate as

$$Mo^{4+}_{(aq)} + 2Na_2SeSO_3 + 4\ OH- \xrightarrow[60\ ^0c\ \pm 2]{pH9.6} MoSe_2 + 2\ Na_2SO_4 + 2H_2O$$

3.2. Optical Absorption Study:

The optical absorption spectra of the deposited MoSe2 in films on FTO coated sustrate was recorded in the wavelength range 350 to 850 nm at room temperature. The optical absorption coefficient of MoSe2 thin films was calculated using the absorbance value measured for a perticalar wavelength(λ) and predetermined values of film thickness(t) using the relation

$$\text{Absorption coefficient}(\alpha) = \text{Optical Density/Thickness(t)}$$

The absorption coefficient was in the order of $10^5 cm^{-1}$confirming the direct allowed transition.

Fig.1 shows a plot of $(\alpha h\nu)^2$ versus $h\nu$. It is linear at higher energies indicates direct type of transition. The extrapolation of straight line portion to zero absorption(α=0) given the band gap energy(Eg) of Molybdenum diselenide to be 1.76 V.

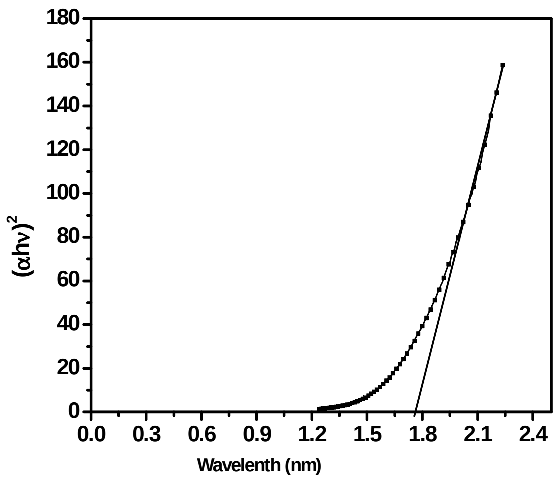


Fig.1. The $(\alpha \hbar\nu)^2$ Vs ($\hbar\nu$) plot for the $MoSe_2$ thin film

3.3 . X-ray Diffraction Studies (XRD):

Fig.2 is the XRD pattern of the $MoSe_2$, thin films on stain less steel substrate at optimized preparative parameters. The sharp peaks reveal the polycrystalline nature with the hexagonal crystal structure. The observed 'd' values are compared with JCPDS data (card No- 15-0029) to determine the crystal structure the observed 'd' values have been found to be in good agreement with standard 'd' values. As shown in table1.

Table .1. Comparison of observed d' values with standard 'd' values for Molybdenum diselenide thin films

Sr No.	Standard 'd' value (A)	Observed 'd' values	(hkl)
1	3.241	3.374	(004)
2	2.149	2.100	(006)
3	1.303	1.282	(204)
4	1.075	1.096	(0012)
5	1.044	1.049	(213)

The crystallite size was calculated from the full-width at half-maximum (FWHM) measurement for the prominent X-ray diffraction peaks using Scherer formula[8].The crystallite size (grain diameter), D, of the deposits was calculated using the Scherrer formula for the (006) peak assuming that microstrain can be neglected.

$$D= k\lambda /\beta \cos \theta$$

Where, D is the crystallite size
k Constant varies with hkl and crystallite shape but usually nearly equal to 0.94
λ Wavelength of source radiation.
β Full-width at half maximum of the peak, in radian.
θ Bragg's angle.

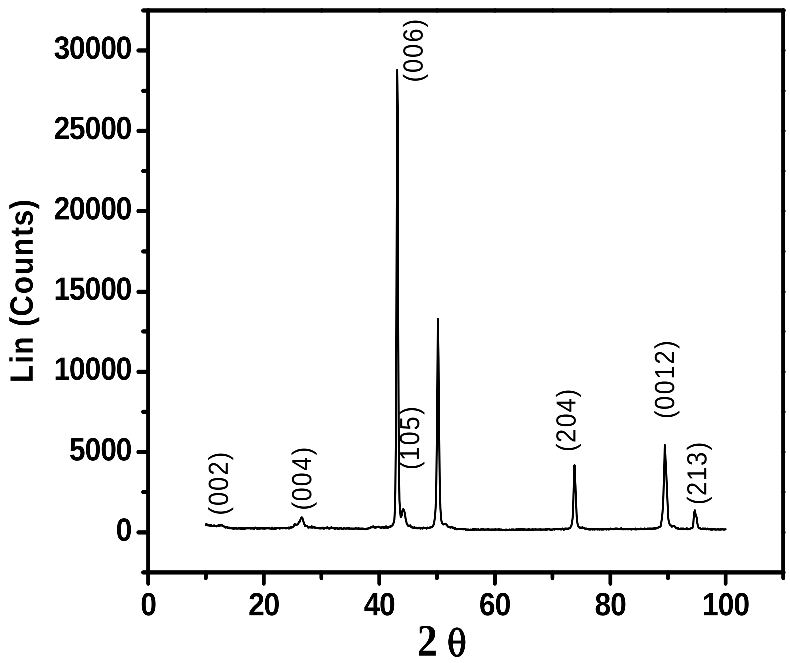


Fig.2.-XRD pattern of the $MoSe_2$ thin film

3.4 The Scanning Electron Microscopy (SEM):

The scanning electron micrograph of $MoSe_2$ thin film given bellow shows well adherent uniform deposition of the material over substrate. The smooth and uniform, adherent film surface without cracks feature observed in low magnification observation it has shown high mechanical stability of the films [9]. The top view showing scanning electron micrograph of the thin film of materials $MoSe_2$ is shows in Fig.3.It shows typical SEM micrograph of $MoSe_2$ thin films. The SEM of $MoSe_2$ shows a typical morphology looks like beads. This micrograph is taken at magnification 10,000X, the compactness of the film itself indicate that it is suitable for the absorption of the solar radiations considerably.

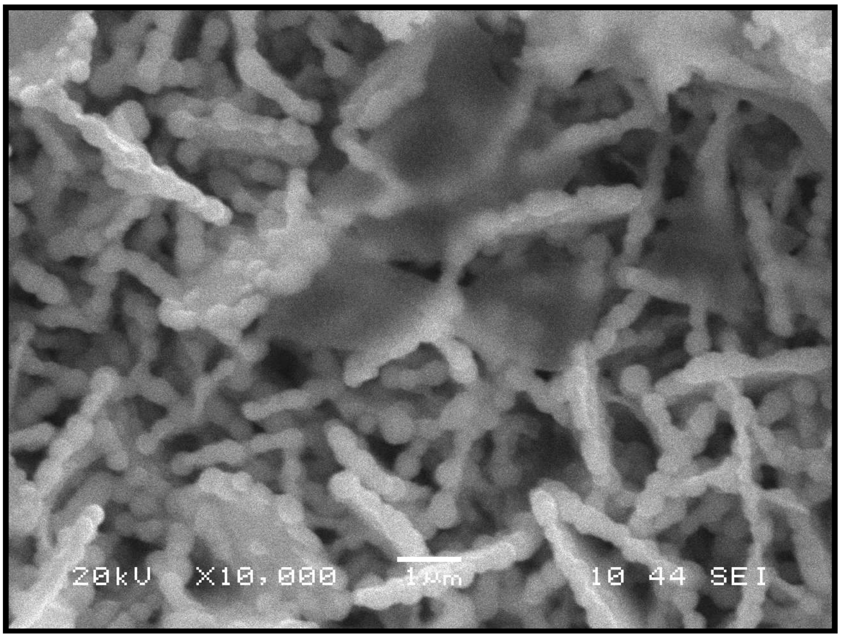


Fig.3. SEM micrograph of $MoSe_2$ thin film

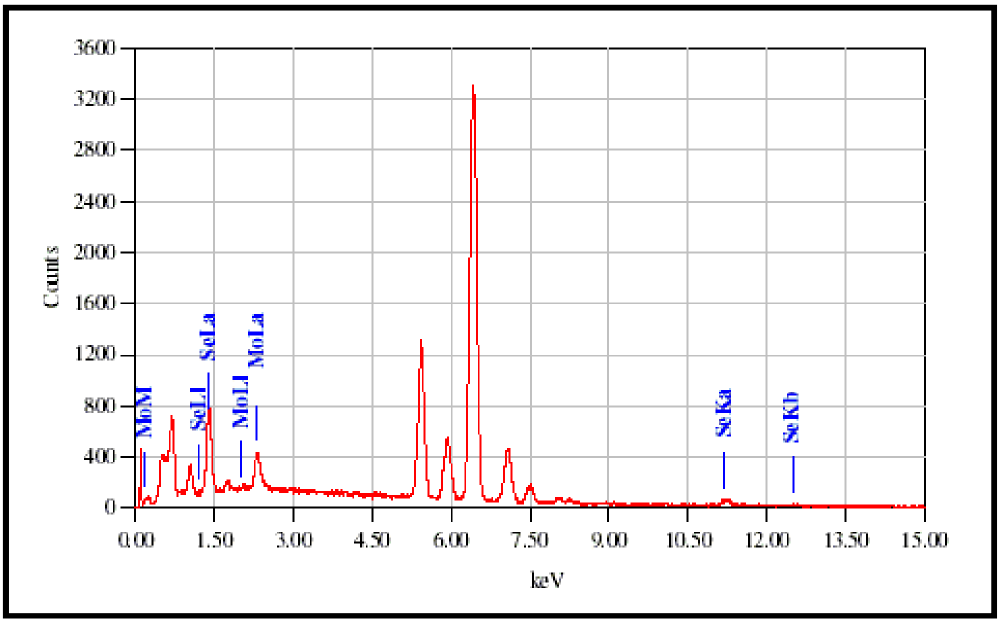
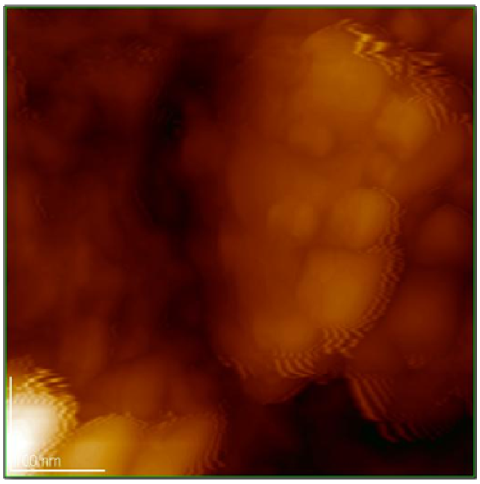
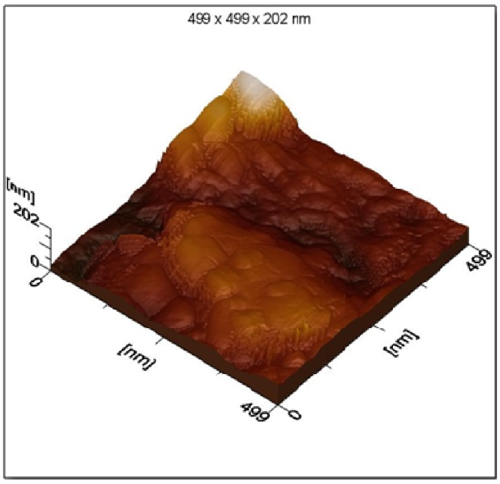


Fig.4. The EDS scanning pattern of the $MoSe_2$ thin films

3.5 . Energy Dispersive Spectroscopy (EDS):

The Binary transition metal dichalcogenide thin films synthesized by chemosynthesis route were analyzed using EDS technique. The quantitative analysis for energy dispersive X-ray analysis was performed on a JEAOL-JSM-6360A scanning microscope. The films were cut into $1cm^2$ pieces and mounted on the sample holder with conducting paste. The samples were coated with a thin layer of platinum to prevent charging of the samples. For comparative studies, the electron beam was kept constant while analyzing the samples. The EDS spectrum obtained with an accelerating voltage of 20KV, acquisition time of 1 minute on a film within the precision of the energy dispersive X-ray analysis, i.e. ± 2%. The EDS spectrum of $MoSe_2$ sample is shown in Fig.4. From EDS data it is observed that the atomic percentage of Mo and Se is in the ratio of 1:2





a **b**

Fig.5. AFM Micrographs $MoSe_2$ thin film i) Two Dimensional a ii) Three Dimensional b

3.6. Atomic Force Microscopy (AFM):

AFM studies were carried out using JEAOL-JSM microscope to find the surface morphology of the resulting films. The micrograph of the surface obtained by AFM shows the good adhesion of the films to the substrate. It shows that the films are uniform and pin-hole-free as seen in the Fig. 5 two dimensional and three dimensional micrographs of the film surface. The grain size is found to be in the range of 100-300nm. This is in good agreement with the grain size values observed from the SEM studies.

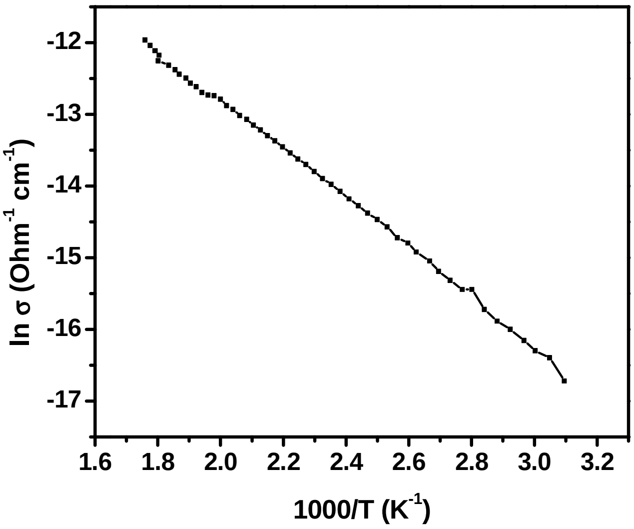


Fig.6. In σ Vs 1000/T (K^{-1}) plot for chemically deposited $MoSe_2$ thin film

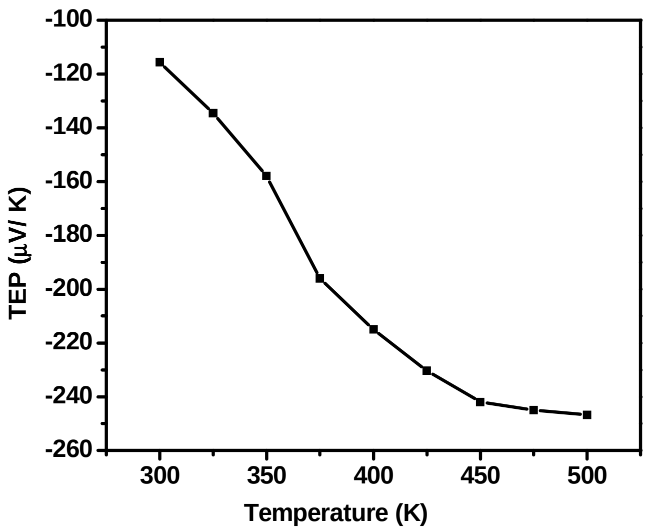


Fig. 7. Temperature dependence of the thermoelectric power for chemically deposited $MoSe_2$ thin film

3.7 Electrical transport Studies:

The study of electrical conductivity was carried out by using two point D.C.probe technique by varying the temperature from 300K to 500K. The electrical conductivity of $MoSe_2$ film at room temperature was found to be of the order of $10^{-4}\ \Omega^{-1}cm^{-1}$. The low value of electrical conductivity may be attributed to nanocrystallinity of film, presence of surface states, small thickness of the film etc. The electrical conductivity increases exponentially with increasing temperature Fig. 6, hence follows the typical trend for semiconductor. According to Arrhenius law for thermally activated conduction ($\sigma = \sigma_o \exp(-\Delta E_a/k_B T)$, where ΔE_a is the activation energy), i.e., plotting ln σ with 1/T results in a linear curve with a slope of $-\Delta E_a/k_B$. Here we obtained activation energy of 0.61 eV.

The nature of charge carriers in these materials was probed with thermolelectric power measurements as a function of temperature. The temperature dependence of Seebeck coefficient of $MoSe_2$ film is shown in Fig.7.The Seebeck coefficient (thermopower) of thin film was determine from the plot of the measured seebeck voltage versus the temperature difference across the specimen($S=\Delta V/\Delta T$) [10-12]. The Seebeck coefficients are negative in value and this indicates electrons as main carriers. The smooth variation of Seebeck coefficient at low temperatures can be attributing to the high carrier concentration [13].

CONCLUSION

The transition metal dichalcoginide $MoSe_2$ thin films were prepared APT and characterised for optostructural, morphological and electrical studies. The UV-Vis-spectra of the films gave band gap values Eg=1.76 eV. The SEM and AFM micrographs gave surface morphology of the films. It revealed that films are compact uniform and adherent with pin-hole-free nature. The EDS studies revealed composition of the films is stoichiometric. The compositions found were in proportion as 1:2.

REFERENCES

[1] G.Lucovsky, R.M. White, J.A. Bendaand J.F. Revelli: *Physi.Rev*.137 (**1973**)3859
[2] E. Bergmann, G.Melet, C.Mucilerand A.Simon. *Vermot Tribol. Int* 28(**1981**)329.
[3] P.Niederhauser,H.E.Huntermann and M.MILLAT *Thin Solid Films*108(**1983**)209
[4] Krishana C. Mandal And Oumarou Svadogo: *J. OF Mater. Chem*.,1,(**1991**),301-302.
[5] N. S. Patil, A. M. Sargar, S. R. Mane, P. N. Bhosale, *Applied Surface Science* 254 (**2008**) 5261-5265
[6] B. D. Ajalkar, S. H. Burungale, D. S. Bhange, P. N. Bhosale, *J. Mater. Sci*., 39 (**2004**) 1659-1664.
[7] N. S. Patil, A. M. Sargar, S. R. Mane, P. N. Bhosale, *Appl. Surf. Sci*., 254 (**2008**) 5261-5265.
[8] V Bilgin, I Akyuz, S Kose and F Atay, *Semicond. Sci. Technol*., 21 (**2006**) 579-585.
[9] D. Zhang, T. Yashoda, H. Minoura, *Adv. Mater*., 15 (**2003**) 814.
[10] W.J. HICKS, *J. Electrochem. Soc*.111 (**1964**) 1058.
[11] E. Revlonsky and D.J. Beernsten, *J.Appl, Phys*. 35 (**1964**)2086.
[12] J.A. Champion; *Brit. J. Appl. Phys*., 16 (**1965**) 1035-1037.
[13] S. Kumar, S. C. Kashiap, K. L. Chopra, *J. Non-Cryst. Solids*. 85 (**1986**) 100.