

Micro-Crystallographic, Optical and Transport Studies of Cd_{0.7} Zn_{0.3} Se : Sb Thin Films

D. S. SUTRAVE, G. S. SHAHANE

DBF Dayanand College of Arts and Science, Solapur 413002, M.S. INDIA

V. B. PATIL, L. P. DESHMUKH

Thin Film and Solar Studies Research Laboratory,

Department of Physics (Appl. Electronics),

Shivaji University Centre for P. G. Studies, Solapur 413003, M. S., INDIA

B. D. SARWADE

Polymer Chemistry Division National Chemical Laboratory Pune, M.S. INDIA

Received 17.06.2000

Abstract

Cd_{1-x}Zn_xSe thin film structures doped with various concentrations of trivalent antimony were chemically deposited onto glass-substrates. These structures were then characterised through the XRD, SEM, optical and electrical characterization techniques. The X-ray diffractograms of both as-prepared and Sb-doped samples were obtained and analysed. The analysis revealed that the samples are microcrystalline over the whole range of the doping concentration (0 to 2 mol %). It is striking that the intensities of hexagonal and cubic reflections of CdSe went on increasing with doping concentration upto 0.1 mol % and decreased with further increase in Sb³⁺ content in the film whereas peak intensities corresponding to cubic ZnSe remained almost constant. The optical studies showed a little shift in the absorption edge, typically from 600 nm to 650 nm for the change of Sb concentration from 0 to 0.1 mol % . The optical transitions are found to be of the direct type with the values of m nearly 0.5 for all films.

The electrical transport studies showed increase in the conductivity with doping concentration up to 0.1 mol % and the conductivity decreased for further increase in the doping concentration. Typically the conductivity improved by an order at 450 K whereas these changes are more significant at around 300 K. The thermo-power measurements gave n-type conduction of the samples and the variation of thermoelectric power with temperature is nonlinear. Other film characteristics, namely activation energy of an electrical conduction, carrier concentration, mobility and intercrystalline barrier potential, were determined from these observations and their temperature and composition dependence have been examined.

1. Introduction

Mixed metal chalcogenides are attracting a great deal of attention because of their many fold importances in a wide spectrum of optoelectronic devices. Chalcogenides of II-IV , IV-VI , II-IV-VI and I-III-VI families have already emerged as the candidates of high potential and performance and low production cost. Their high coefficient of an optical absorption and nearly matching bandgaps with the active region of the solar spectrum are the basis for them being much popularity in a variety of optoelectronic and conventional storage devices [1-4] . Cd_{1-x}Zn_xSe is one such semiconductor whose energy gap can be engineered to cope with the electromagnetic spectrum and therefore many of the optoelectronic properties can be controlled smoothly making it convenient for use in radiation detection, projection colour TV's and in photoelectrochemical cells. CdSe is now proved to be one of the best base materials used in photoelectrochemical applications and that

incorporation of zinc into it has shown pronounced effect in enhancing the electrochemical conversion efficiency [5-8]. Additionally, purpose of the Sb^{3+} doping is to reduce the electrical resistivity of the photoactive material that would increase the short circuit current and hence ultimately enhance the conversion efficiency. Addition of the trace amount of the dopants into various hosts so as to improve the structural, optical and electrical transport properties, has been reported by number of workers [9-12]. Our main intension is to employ this material for fabrication of the electrochemical devices and therefore, it is worth to examine its above mentioned properties when it is activated by means of an Sb^{3+} trivalent impurity.

2. Experimental Techniques

2.1. Deposition of the samples

The $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Se}:\text{Sb}$ thin film layers were prepared in an alkaline medium by a chemical deposition method [4,5,8]. The substrates used were ultracleaned glass microslides. Equimolar solutions of cadmium sulphate and zinc sulphate in appropriate volume were complexed together by means of triethanolamine and ammonia. The Se^{2-} ions were provided to the bath externally by adding sodium selenosulphate at a constant rate. Antimony trichloride (A.R.grader was used as a source of dopant material and was varied such that the concentration of Sb^{3+} in the thin film structure was varied from 0.01 mol % to 2 mol % [11]. The reaction was carried out at a pH value around 10 ± 0.2 . Sodium hydroxide was used to control the pH value. The bath temperature was then raised to 70 ± 2 °C and the substrates assembled on a substrate holder were kept rotating at 70 ± 2 rpm speed in the reaction mixture This allows for a constant and continuous mechanical churning of the bath solution.

2.2. Characterisation of the samples

The film thickness was measured by a weight difference method. The XRD traces were obtained using a Philips PW-1710 X-ray diffractometer with $\text{CuK}\alpha$ (1.5406 \AA) line. The range of 2θ angles was from 10° to 80° . The surface topography of these samples was examined through a scanning electron microscope. The optical density was measured for all the samples in the 300 nm to 900 nm wavelength range using a double beam spectrophotometer (Hitachi - 330 Japan) The dark dc electrical conductivity was measured in the 300-600 K temperature range. Silver paint was used as a contact material. The thermo emf's generated by the samples were noted in the 300- 550 K temperature range. The carrier concentration and mobility and intercrystalline barrier heights were determined from these studies.

3. Results and Discussion

3.1. $\text{Cd}_{0.7}\text{Zn}_{0.3} \text{Se} : \text{Sb}$ thin films : Physical observations

As-grown and Sb-doped $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Se}$ samples were thin, uniform diffusely reflecting and tightly adherent to the substrate surface. The yellowish-red colour of the sample went on faint as concentration of Sb^{3+} was increased. The terminal thickness of the film was measured and listed in Table. An increase in film thickness with antimony doping concentration upto 0.1 mol % Sb has been observed. At still higher doping concentration, the thickness decreased. The initial increase and then decrease of film thickness with antimony doping concentration could be justified on the basis of role of the antimony atom as a nucleation centre [4,5]. Basically, film thickness is a very sensitive function of the various preparative parameters (such as deposition time and temperature, pH of the reaction mixture, molar concentrations of the basic reactants, speed of the rotating substrates, effective Zn concentration in the film, doping concentration etc). In our studies, all other parameters (except Sb-doping concentration) were kept at their optimum values [11] and the films were doped with a varying antimony doping concentration. When the glass substrates are dipped in the triethanolamine complex formed by cadmium and zinc salts, a suspension of this complex that acts as a catalytic surface forms a thin layer on it that decomposes sodium selenosulphate resulting in a (Cd, Zn)Se film formation. Nucleation initiates at and around Sb^{3+} in a complex suspension which then contributes

to the enhancement in the film formation process up to 0.1 mol % antimony doping level Beyond which antimony acts as impurity charge scattering centre thereby preventing the further film growth. [5,11,12].

3.2. Cd_{0.7}Zn_{0.3}Se : Sb film studies

a) X-ray diffraction studies

X-ray diffraction studies were carried out on these samples in the range of angles between 10° to 80° and the diffractograms were analysed to obtain the information about various crystallographic aspects. The diffractograms of Sb-doped Cd_{0.7}Zn_{0.3}Se samples are shown in Fig. 1 . The patterns suggest that the as-deposited films are polycrystals and the crystalline nature is found to be enhanced upto 0.1 mol % Sb-doping concentration and thereafter it decreased. The doped film structures are composed of hexagonal and cubic CdSe and cubic ZnSe phases with few reflections of Sb₂O₃ and elemental Sb [11]. The reflected intensity of the most intense peak (101) of hexagonal CdSe is increased as the Sb-concentration is increased from 0.01 mol % to 0.1 mol % . For further increase in Sb-content intensity decreased suddenly to about 50 % and remained more or less constant (Fig. 2a). Similar intensity variation is also observed for (102) hexagonal reflection of CdSe. While for ZnSe (220) the peak intensity is found to be more or less constant. Above discussion revealed that incorporation of antimony into Cd_{0.7}Zn_{0.3}Se resulted into improvement in the crystallinity upto 0.1 mol % Sb-concentration and for higher values of Sb content (> 1 %) particle size reduces and the films tend towards amorphous [11]. The particle size was determined from the XRD analysis and Fig 2(b) shows its variation with the Sb-doping concentration. It is observed that the particle size is larger at 0.1 mol % Sb-concentration in Cd_{0.7}Zn_{0.3}Se film [11].

Table Effect of Sb- doping concentration on various properties of the Cd_{0.7} Zn_{0.3} Se thin films.

Sr. no.	Sb-doping mol %	Thickness μ m	power factor m	Activation energies	
				H.T. eV	L.T. eV
1	0.0	0.55	0.60	0.69	0.13
2	0.01	0.56	0.60	0.69	0.13
3	0.025	0.57	–	0.66	0.11
4	0.05	0.60	0.46	0.65	0.11
5	0.075	0.62	0.40	0.64	0.12
6	0.1	0.65	0.43	0.63	0.11
7	0.15	0.62	–	0.65	0.11
8	0.2	0.59	0.50	0.67	0.11
9	0.5	0.50	0.44	0.70	0.13
10	1.0	0.40	0.40	0.72	0.14
11	2.0	0.40	0.48	0.76	0.13

b) SEM studies

The SEM micrographs of few of the Sb-doped samples were taken to support the XRD observations. Fig. 3 shows the SEM micrographs showing surface topography of five representative Sb-doped samples. From the micrographs it is clearly seen that the particle size is improved considerably up to 0.1 mol % and thereafter decreased [11]. All the micrographs show diffused grains and are spherical in shape. The grains of the doped samples are more clear whereas pure a sample shows some overgrowth on the spherical grains. The overgrowth for 0.1 mol % Sb-doped sample is more and also the grains appear larger in size with reduced intergrain spacing. At higher doping levels, grains become separate with increased intergrain spacing. At still higher doping levels particle size is reduced significantly showing crystalline to amorphous phase transition of the material without any overgrowth observed [11]. Such type of overgrowth has been reported by Bhushan and Srivastav [13] and Deshmukh and Shahane [14].

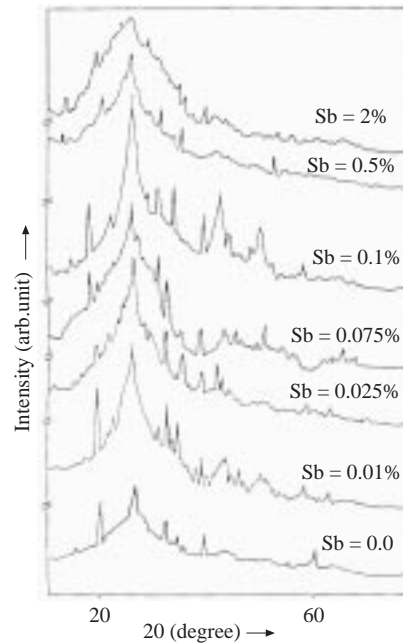


Figure 1. The X-ray diffractograms of seven typical Sb-doped $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Se}:\text{Sb}$ thin films.

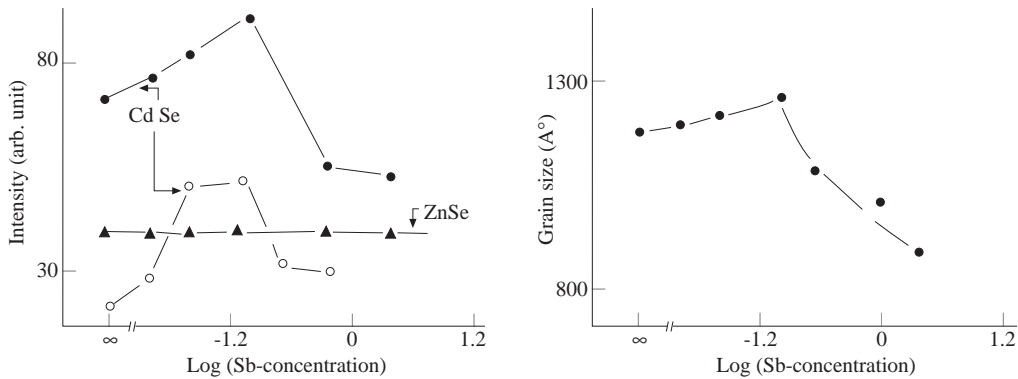


Figure 2. 2a) Effect of Sb-doping concentration on intensities of (●) 101 Hexagonal plane, (○) 102 Hexagonal plane, (▲) 220 Cubic plane. 2b) Variation of grain size with Sb-doping concentration.

c) Optical studies

The optical absorption measurements were recorded on both undoped and Sb-doped $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ ($x = 0.3$) layers in the 350 nm to 900 nm wavelength range. The absorption coefficient was calculated for all the compositions. The magnitude of α is high ($\cong 10^4 \text{ cm}^{-1}$) and a shift in the absorption edge, typically from 600 nm to 650 nm has been observed for the change of antimony doping from 0.01 mol % to 0.1 mol % . The data were used to calculate the optical gaps of these films by plotting $(\alpha h\nu)^2$ vs $h\nu$ curves. Fig. 4. is a sketch of the optical gap versus Sb-doping concentration. The energy gap is decreased a little, typically, from 2.1 eV to 1.9 eV for the variation of Sb-content from 0.01 mol % to 0.1 mol % . The decrease in the bandgap could be ascribed to the improved grain structure of the films due to the segregation of the impurity atoms along the grain boundaries [13-15] whereas, increase in the band gap at higher doping levels (1.90 eV to 2.2 eV) may be due to the increased amount of disorder caused by the addition of impurity [13-15].

The mode of optical transitions in these films is of the band to band direct type. This has also been confirmed by plotting $\ln(\alpha h\nu)$ vs $\ln(h\nu - E_g)$ for direct allowed type transitions. The variation should yield a straight line with slope (power factor) equal to 0.5. The values of m are documented in Table.

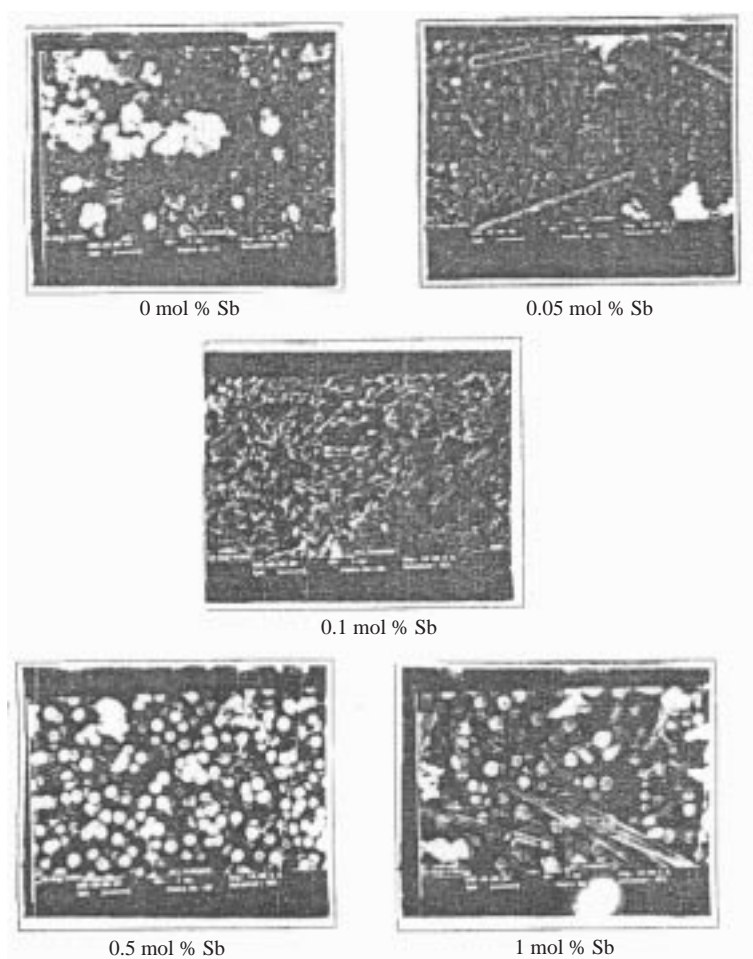


Figure 3. The SEM micrographs of $Cd_{1-x}Zn_xSe$ thin films with variations in Sb-doping concentrations.

d) Electrical transport studies

i) Electrical conductivity

The dc electrical conductivities of the Sb-doped $Cd_{0.7}Zn_{0.3}Se$ samples in dark, in the range of working temperature from 300 K to 600 K, were measured. The temperature activated electrical conductivities are shown in Fig. 5 for six typical compositions. The plots exhibit two distinct regions corresponding to two values of the activation energies (listed in Table). It is found that the conductivity increased systematically with increase in the antimony doping concentration upto 0.1 mol %, which can directly be understood from the role of Sb^{3+} as donor and improvement in the crystallite sizes [13]. Improvement in the crystallite size results in the decreased intergrain boundary potential because of the reduced number of incomplete atomic bondings which in turn reduces the number of charge trapping centres, [11,15,16]. Secondly, when $Cd_{1-x}Zn_xSe$ ($x = 0.3$) composites are doped with a trivalent antimony, two processes may take place: i) substitution of a divalent Cd^{2+} / Zn^{2+} ion by a trivalent Sb^{3+} ion and ii) formation of Cd^{2+} / Zn^{2+} vacancies. Since Cd^{2+} , Zn^{2+} and Sb^{3+} were deposited simultaneously, there is a less chance for forming the Cd^{2+} / Zn^{2+} vacancies [5,11,17]. Thus the possibility of substitution of a divalent Cd^{2+} / Zn^{2+} by a trivalent antimony is predominant which makes the antimony atom to act as donor [5,15,16,18]. The chemical analysis before and after doping suggest that Sb^{3+} replaces Cd^{2+} rather than Zn^{2+} . This causes electrical conductivity to increase upto 0.1 mol % Sb-concentration. For Sb-concentrations well in excess of 0.1 mol %, the lattice structure becomes more and more distorted which causes grain boundary scattering to increase thereby reducing the carrier mobility and therefore the conductivity. This is shown in Fig. 6. The temperature dependence of an electrical conductivity (Fig. 5) showed an usual Arrhenius behaviour

consisting of high and low temperature regions. Now to check for the type of conduction mechanisms, the plots of $\log(\sigma T^{1/2})$ vs $1000/T$ and $\log \sigma T^{1/2}$ vs $T^{-1/4}$ were constructed [18-21]. Obviously the straight line nature of these plots in the high and low temperature region suggests the grain boundary limited and variable range hopping conduction as the dominant conduction mechanisms. We would like to state that the localised states necessary for such a hopping conduction are the direct consequence of the imperfections associated with the polycrystalline films [11,20,22].

ii) Thermoelectric power

The thermo emf was measured in dark for all the samples in the 300-550 K temperature range. The measurements showed n-type conduction for all the samples. The thermoelectric power (p) of a sample doped with 0.1 mol % Sb is lowest indicating greater number of carriers. For higher doping levels, selenium vacancies would have reduced due to the addition of Sb^{3+} ions, thus lowering the conductivity [11]. This explains why thermoelectric power is higher after 0.1 mol % Sb-doping levels. The carrier concentration for each temperature has been computed for all the films using the standard relation [12].

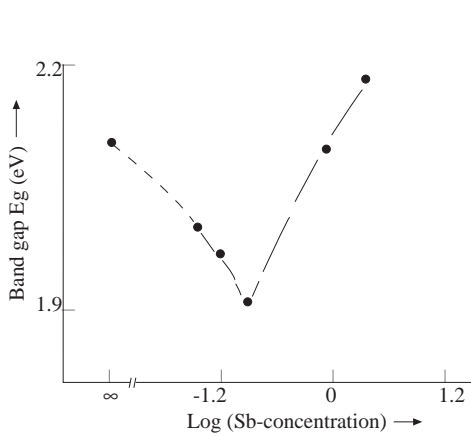


Figure 4. A sketch of band gap with Sb-doping concentration in (Cd, Zn) Se thin films.

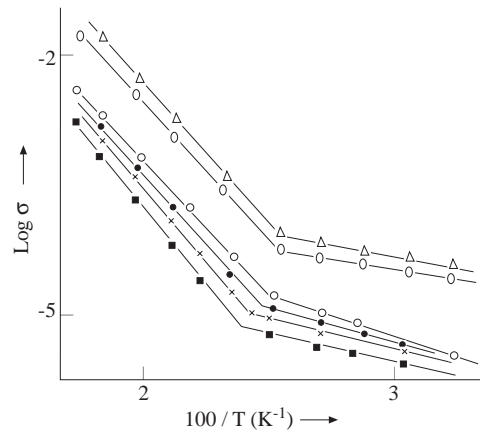


Figure 5. Temperature dependence of an electrical conductivity for $Cd_{0.7}Zn_{0.3}Se : Sb$ films : 0 mol % Sb (●), 0.025 mol % Sb (○), 0.1 MOL % SB (▲), 0.2 mol % Sb (○), 1 mol % Sb (×), 2 mol % Sb (◆).

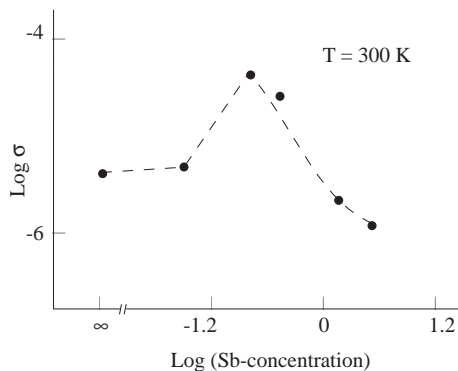


Figure 6. Variation of $\log \sigma$ with Sb-doping concentration.

It is found that the carrier concentration increased as the temperature increased and is little bit higher for the 0.1 mol % Sb-doped sample. On addition of the Sb^{3+} upto 0.1 mol %, carrier concentration increased as expected, since the Sb^{3+} forms shallow donor levels [11,22]. However, at higher doping levels, there is a small decrease in the carrier concentration which may probably be due to the increased disorder that causes an increase in the carrier trapping [11,22]. The carrier mobilities (μ) at various temperatures for all the samples were then determined. It is found that the carrier mobility increased significantly with the Sb-doping

concentration up to 0.1 mol % and then decreased thereafter. The variations in carrier concentration (n) and mobility (μ) with Sb-concentration are shown in Fig. 7. It is seen that the carrier mobility is enhanced significantly which can be correlated to the improved crystallinity of the film (which is also detected from XRD & SEM studies) [11].

The variation in the carrier mobility with Sb^{3+} doping can further be understood from measurement of the intercrystalline barrier height Φ_B . The carrier mobility is thermally activated and has relation with the grain boundary potential which puts a limit on the conduction process. The intercrystalline barrier heights (Φ_B) were therefore calculated from the temperature dependence of mobility. The variation of Φ_B with the doping concentration is shown in Fig. 8. This indicates that Φ_B is smaller for 0.1 mol % Sb-doped sample. For higher doping concentrations, antimony serves as the neutral impurity centres that in turn act as the scattering centres and hence reduce the carrier mobility [11,14-16].

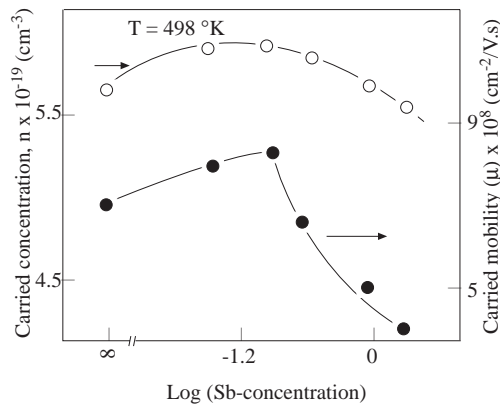


Figure 7. The variation of carrier concentration (n) and mobility (μ) with Sb-doping concentration in $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Se}$ the films.

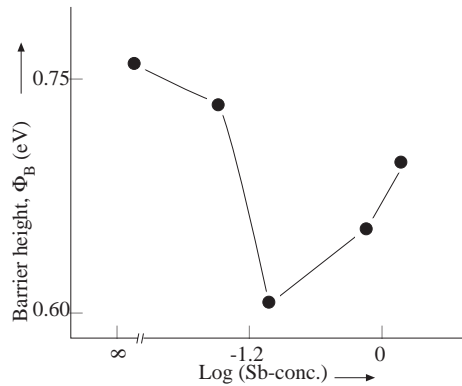


Figure 8. Dependence of grain boundary potential Φ_B on Sb-doping concentration in $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Se}$ structures.

References

- [1] A.H. Burger and M.J. Roth, *Crystal Growth*, **70**, (1989) 386.
- [2] T.M. Razykov, *Thin Solid Films*, **164**, (1988) 301.
- [3] G. Hodes, D. Cahen, J. Manassen and M. David, *J. Electrochem. Soc.*, **127**, (1980) 2252.
- [4] D.S. Sutrave, G.S. Shahane, V.B. Patil and L.P. Deshmukh, *Turkish J. Phys.*, **23**, (1999) 1.
- [5] A.A. Basam, A.W. Brinkman, G.J. Russel and J. Woods, *J. Cryst. Growth*, **86**, (1988) 667.
- [6] R. Chandramohan, C. Sanjeevraja and T.M. Mahalingam, *Phys. Stat. Solid.*, (a) **163**, (1997) 11.
- [7] C. Natrajan, G. Nogami and M. Sharon, *Bull. Electrochem.*, **12**, (1996) 136.
- [8] D.S. Sutrave, G.S. Shahane, V.B. Patil and L.P. Deshmukh, *Ind. J. Pure & Appl. Phys.*, **37**, (1999) 384.
- [9] L.P. Deshmukh, C.B. Rotti and G.S. Shahane, *Ind. J. Pure & Appl. Phys.*, **36**, (1998) 322.
- [10] L.P. Deshmukh, A.B. Palwe and V.S. Sawant, *Sol. Ener. Mat.*, **20**, (1990) 341.
- [11] D. S. Sutrave, B. T. Raut, G. S. Shahane, L. P. Deshmukh and B. D. Sarwade, "Proc. National Seminar on Recent Trends in Material Science" S. V. University Tirupati, India, 25-27, Nov. 1999.
- [12] K. Subramanian and V. Sundar Raja, *Sol. Ener.Mat. and Sol.Cells.*, **32**, (1994) 1.
- [13] S. Bhushan and S. Srivastav, *Ind. J. Pure & Appl. Phys.*, **33**, (1995) 371.
- [14] G.S. Shahane and L.P. Deshmukh, *Mat. Chem. Phys*, **51**, (1997) 246.

- [15] L.P. Deshmukh, B.M. More, S.G. Holikatti, *Bull. Mater. Sci.*, **17**, (1994) 455.
- [16] J. Rodriguez and G. Gordillo, *Sol. Energ. Mater.*, **19**, (1989) 421.
- [17] S. Jatar, A. C. Rastogi and V. G. Bhide, *Pramana*, **16**, (1978) 477.
- [18] J.Y. W. Seto, *J. Appl. Phys.*, **46**, (1975) 5247.
- [19] J.W. Orton and M. J. Powell, *Rep. Progr. Phys.*, **43**, (1980) 1263.
- [20] H.F. Mott, *Phil. Mag.*, **19**, (1969) 835.
- [21] Y. Natsume, H. Sakata and T.Hirayama, *Phys. stat. Solidi (a)*, **148**, (1995) 485.
- [22] L.I. Soliman, *Ind. J. Pure & Appl. Phys.*, **32**, (1994) 166.