

Chemically Synthesized (Cd, Hg)Se Pseudobinaries: Some Characteristic Properties

V. B. PUJARI

*Rayat Shikshan Sanstha's, Modern College, Vashi, Navi-Mumbai 400703, M. S., INDIA
e-mail: vbpujari2002@rediffmail.com*

V. B. GAIKWAD, E. U. MASUMDAR, P. D. MORE and L. P. DESHMUKH*

*Thin Film and Solar Studies Research Laboratory, Department of Physics,
Shivaji University Centre for P. G. Studies, Solapur – Pune Road, Kegaon, Solapur
413002, M. S., INDIA*

Received 29.08.2001

Abstract

This paper presents some information regarding (Cd, Hg) Se materials synthesized by a simple chemical growth process and the structural, optical and electrical transport properties. The growth of these films depends on various preparative parameters and deposition conditions such as concentration of the starting materials, pH, temperature, time, speed of mechanical churning, etc., and the reaction kinetics suggests that the films grow into two different phases: one, initially an almost linear phase; and second, a saturation phase. The deposits were analysed chemically and by an EDS techniques. It has been seen that more than 70% of the materials taken in the reaction bath get deposited on the substrate. The variation of x_{film} with x_{bath} is nonlinear. The as-deposited films consists of crystals of hexagonal wurtzite and cubic zinc blend phases of both CdSe and HgSe. The optical absorption studies revealed a high absorption coefficient ($10^4 - 10^5 \text{ cm}^{-1}$) with direct type of transitions. The estimated band gap follows a nonlinear decay, typically from 1.72 eV to 1.06 eV, as the composition parameter x (Hg-content) was varied from 0 to 0.2. The structural and optical studies showed that the solid solution of the kind $\text{Hg}_x\text{Cd}_{1-x}\text{Se}$ is observed for the values of x ranging between $0 \leq x \leq 0.05$. The dc electrical conductivity is found to increase continuously with an increase in the composition parameter x up to 0.05 and remains more or less constant for higher values of x . The material exhibits both grain boundary scattering limited and a variable range hopping conduction mechanisms. The thermoelectric power is negative showing n-type conduction of the samples. Both carrier concentration n and mobility μ were determined from these studies and found to be dependent on the temperature and film composition.

Key Words: Pseudo-binaries, Chemical synthesis, Optical and transport properties, MCS, Growth Kinetics

1. Introduction

Mercury - Cadmium - Selenide (MCS) is an important class of material because of its electronic and optical properties and potential applications in IR – detection, electro-optic, opto-electric and solar energy conversion devices [1-5]. It has, therefore, been proposed to synthesize $\text{Hg}_x\text{Cd}_{1-x}\text{Se}$ thin films of varying compositions by a simple and extremely convenient solution growth process. An attempt is made on their growth kinetics and the compositional behaviour of the structural, optical and electrical transport properties with the ultimate intension of using MCS thin films in electrochemical conversion.

*Corresponding author

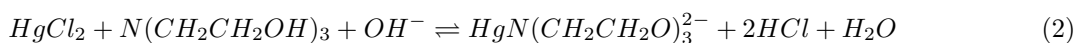
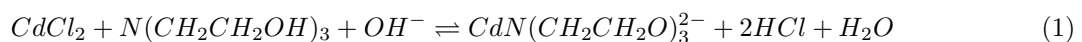
2. Experimental procedure

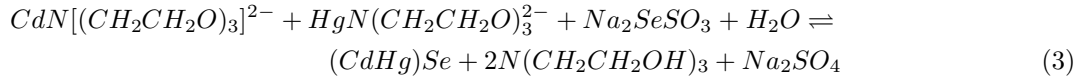
The chemical bath deposition of CdSe and $Hg_x Cd_{1-x} Se$ thin films by co-deposition of Cd^{2+} , Hg^{2+} and Se^{2-} ions in an aqueous alkaline medium is almost inexpensive and simple [6,7]. The starting materials are quite cheap and no sophisticated instrumentation is required. The materials used were cadmium chloride, mercuric chloride and sodium selenosulphite. The Na selenosulphite was obtained by refluxing Se-metal powder (5 g) with anhydrous sodium sulphite (12 g) in 200 ml double distilled water at 80°C for 9 hrs. It was added to the reaction mixture at a controlled rate by a separate arrangement. The deposition parameters such as time, temperature, pH and speed of the substrate rotation were optimized to obtain good quality deposits of controlled compositions. Thus, CdSe and alloyed $Hg_x Cd_{1-x} Se$ thin films were obtained onto the cleaned glass substrates from an aqueous alkaline bath ($pH = 11 \pm 0.5$) consisting of equimolar solutions of the cadmium chloride and mercuric chloride in a definite volume stoichiometric proportion. The solutions were mixed and complexed together with a sufficient quantity of triethanolamine and sodium hydroxide and aqueous ammonia were used to adjust the pH value and film adherence, respectively. Well cleaned glass substrates were mounted on a specially designed substrate holder and rotated in a reaction bath at a 60 rpm speed. This provides a continuous and uniform automatic mechanical churning of the reaction mixture. To obtain good quality samples, the time and temperature of deposition were optimized at 90 min and $60 \pm 2^\circ C$, respectively. The samples were then removed from the reaction bath and the terminal thickness of these as deposited layers were measured by Fizeau interference – fringes technique. The film composition was also determined using the EDS technique. A KEVEX 7000–77 energy dispersive X-ray spectrophotometer was used for this purpose. A chemical spectrophotometric technique was used to determine the actual contents of Cd, Hg and Se ions in both the film and the bath. The X-ray diffractograms of these films were obtained to get the structural information on these films using a Philips PW – 1710 X-ray diffractometer (Cu K α line). The range of 2θ scanning angles was from 20° to 80° . The surface topography was observed through a scanning electron microscope, Cameca, SU–30 (France). A spectrophotometer, Hitachi 330 (Japan) was used to measure the optical absorbance of the samples in the wavelength range from 400 nm to 1300 nm. The coefficient of absorption α , optical gap Eg and the type of transitions were determined from these studies. The samples were then characterized through the electrical conductivity and thermo power measurement techniques. The range of working temperature was from 300 to 600 K. Silver paint was used for making the ohmic contacts. The current and voltage measurements were carried out with a HP - 6 $1/2$ digit and HIL - 4 $1/2$ digit multimeters. A chromel–alumel thermocouple was used to sense the working temperature. The activation energies, carrier concentration, mobility and grain barrier potentials were determined from these measurements and their variations with the film composition have been studied.

3. Results and Discussion

3.1. Growth kinetics and physical observations

This paper is an account of the technical know-how's involved in the process of deposition of the $Hg_x Cd_{1-x} Se$ thin films by a chemical growth technique and few of its materials characteristics. The deposition process is based on co-deposition of Cd^{2+} , Hg^{2+} and Se^{2-} ions which is made energetically favorable by interaction of the ions from the solution with the substrate surface. The films grew by a nucleation process involving an energetic - atomistic condensation of the ions on the substrate to form $Hg_x Cd_{1-x} Se$ nuclei which then grew in size by adsorbing more and more ions from the reaction bulk. The controlled rate of arrival of Cd^{2+} , Hg^{2+} and Se^{2-} ions on the substrate surface from the solution bulk controls the rate of film formation and consequently its growth rate. This has been accomplished by adding an appropriate quantity of triethanolamine as a complexing agent into the reaction bath that provides an adequate alkaline medium. The fundamental chemical reaction can be formulated as:





At about ambient temperature (~ 300 K), the films are difficult to obtain because of the fact that most of the ions are not free for the reaction to take place. At temperatures above room temperature, an increasing number of ions are set free from the bound complex state and are made available for the reaction. Thus a desired film growth is expected. This is true up to a deposition temperature of about 60°C . Beyond this temperature, more and more ions will come out of the bound complex state and not all the ions will get sufficient time and chance to adsorb on the substrate surface consequently they settle down at the bottom of the reaction container, thus decreasing the layer thickness as shown in Figure 1a. The time dependence of film growth is shown in Figure 1b. It appears that the film growth is almost linear initially and then the thickness saturates for higher deposition periods. For smaller deposition periods, more and more ions will get condensed on the substrate surface showing the layer thickness to increase almost linearly. At larger deposition times, the reaction solution bulk will be depleted of the ionic species and this will continue till a terminal layer thickness is reached. The optimum deposition time selected is 90 minutes. Figure 2 shows the variation of film thickness with the composition parameter x . It is seen that the terminal layer thickness decreased non-linearly with the film composition and could be explained as usual [8]. The as-deposited samples are thin, uniform, smooth, mechanically hard and diffusely reflecting. The colour of the deposits changed from dark orange-red to lead-gray as x was varied from 0 to 0.2. The change in colour with the increased film composition parameter is suggestive of the substitution of Cd^{2+} by Hg^{2+} in the CdSe lattice.

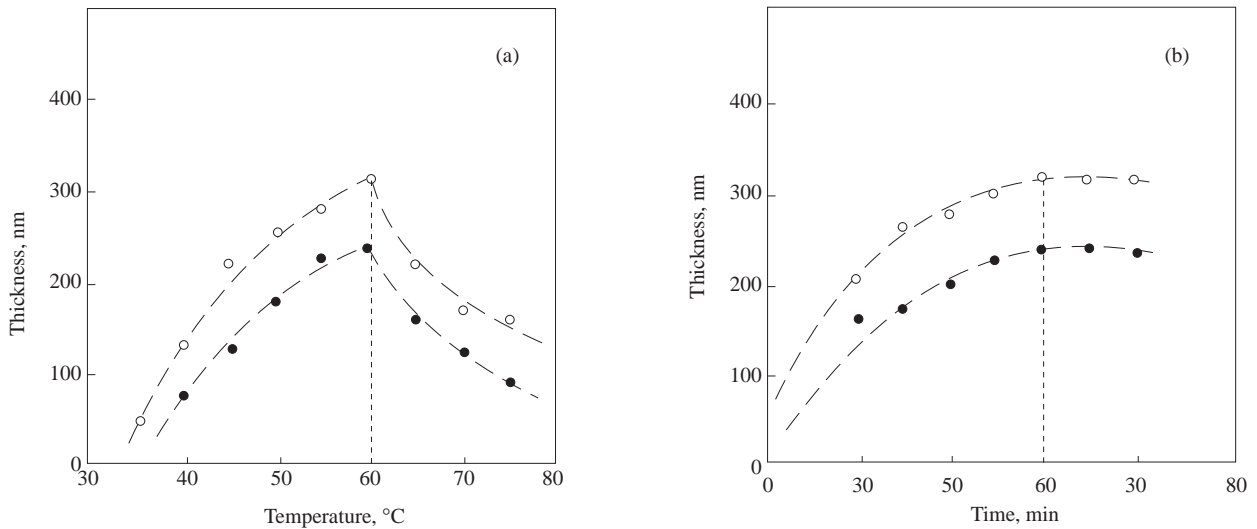


Figure 1. Kinetics of $Hg_x Cd_{1-x}Se$ film growth for $x = 0$ (\circ) and $x = 0.02$ (\bullet): (a) the terminal layer thickness versus deposition temperature, and (b) film thickness versus deposition time.

3.2. The compositional analysis

The film composition was determined by EDS technique. It is found that, as the mole content of Hg in the solution was increased, the Hg-content in the film increased and the corresponding Cd-content decreased. The variation of the composition parameter, x_{film} with x_{bath} , showed non-linear behaviour as shown in Figure 3.

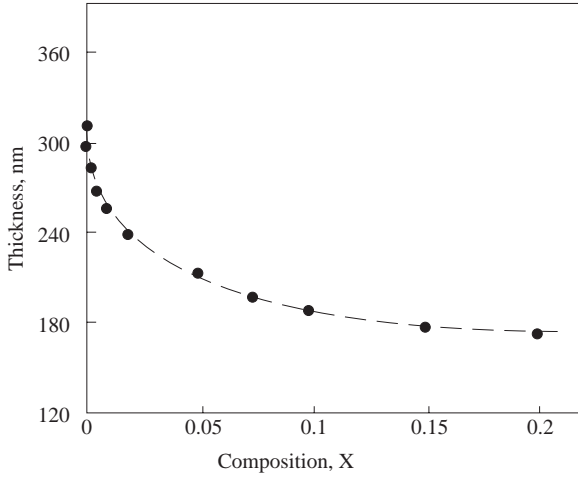


Figure 2. Film thickness versus composition parameter, x ($0 \leq x \leq 0.2$)

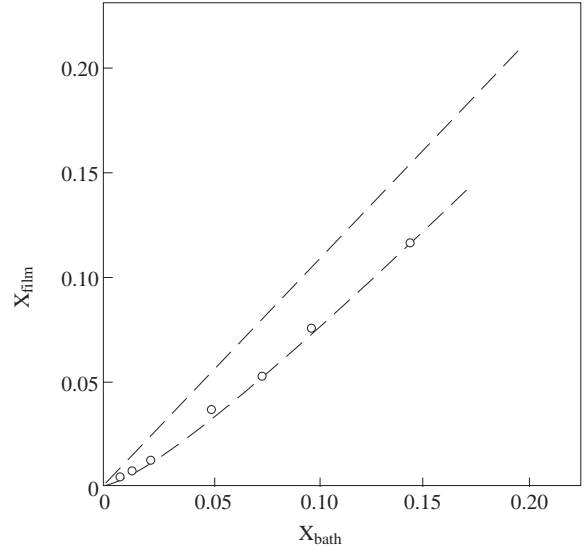


Figure 3. Variation of x_{film} with x_{bath} for $Hg_x Cd_{1-x}Se$ films.

3.3. The structural investigations

The crystal structure of these composite layers was examined with the (2θ) range from 20° to 80° . The samples are of the ternary / alloyed type $Hg_x Cd_{1-x}Se$ polycrystals with the hexagonal wurtzite (dominant) and cubic zinc-blend structures (upto $x \cong 0.05$ mol% Hg). Beyond $x = 0.05$ mol%, separate phases of both CdSe and HgSe have been formed. The lattice parameters were then determined for the dominant hexagonal phase and it is seen that both a and c slightly increases with x nonlinearly for the solid solution region as shown in Figure 4. The average crystal size was determined for all the composite films and are documented in Table 1. It is seen that crystal size increased with increase in Hg-content and tends to be more or less the same for higher Hg-concentrations in CdSe.

Table 1. Some characteristics of $Hg_x Cd_{1-x}Se$ thin film structures.

Composition parameter x	Power factor m	Activation energy $E_{a\sigma}$, eV		Barrier potential ϕ_B , eV	E_{an} eV	Grain size from XRD, \AA
		H.T	L.T			
0	0.41	0.68	0.23	0.60	0.08	177
0.0025	0.43	0.64	0.20	0.54	0.10	183
0.005	0.42	0.59	0.18	0.51	0.08	189
0.0075	0.50	0.57	0.15	0.49	0.08	196
0.01	0.40	0.54	0.137	0.42	0.12	203
0.02	0.48	0.52	0.113	0.41	0.11	218
0.05	0.45	0.49	0.07	0.39	0.10	258
0.075	0.46	0.45	0.05	0.38	0.07	253
0.1	0.42	0.42	0.037	0.37	0.05	247
0.15	0.49	0.39	0.01	0.36	0.03	249

3.4. Optical properties

The optical absorption spectra of these samples were obtained and evaluated to determine the absorption coefficient α for various x values, Figure 5 shows variation of the absorption coefficient, α with x for four typical wavelengths. It is seen that α is maximum at a value of x equal to 0.01 mol% Hg in CdSe. The optical gaps were determined for all the compositions from the absorption spectra. Figure 6 shows variation of the bandgap E_g with film composition x . The variation is monotonic and non-linear. The type of optical

transitions is of the band to band direct type. This is also confirmed by plotting $\ln(\alpha h\nu)$ vs $\ln(h\nu - E_g)$ as suggested by Pal *et al.* [9]. The plots are straight lines with slopes nearly 0.5, suggesting direct mode of transitions. The values of slopes are documented in Table 1.

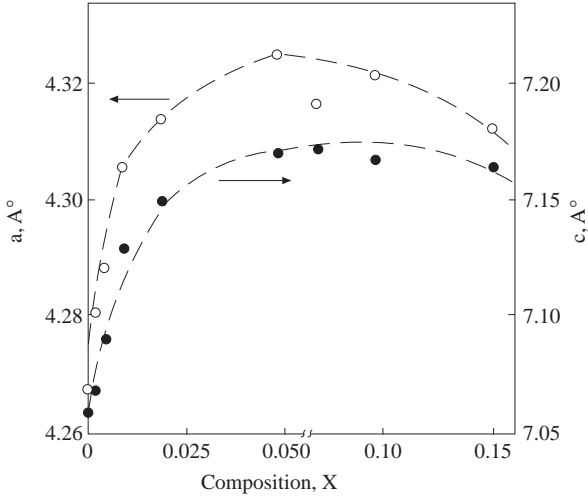


Figure 4. Variation in lattice parameters **a** and **c** with the film composition.

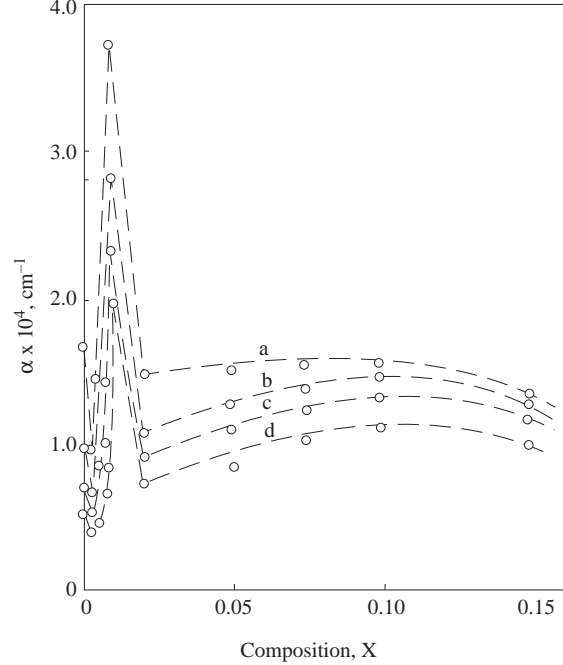


Figure 5. Variation of an absorption coefficient α with the composition parameter x for four typical wavelengths a) $\lambda = 600$ nm, b) $\lambda = 700$ nm, c) $\lambda = 800$ nm d) $\lambda = 900$ nm.

3.5. Transport characteristics

The mechanism of electrical conduction in these films was examined through the electrical conductivity and thermoelectrical power measurements. The dc electrical conductivity of all the samples was therefore measured in the 300-600 K temperature range. The plots of $\log\sigma$ vs $1/T$ exhibit Arrhenous behaviour and the activation energies of an electrical conduction, in both low and high temperature regions, were calculated. These are listed in Table 1. The conduction mechanism involved in these films was examined by plotting $\log\sigma T^{1/2}$ vs $1/T$ and $\log\sigma T^{1/2}$ vs $T^{-1/4}$ as suggested by Micocci *et al.* [10] and Petritz [11]. It has been seen that a variable range hopping conduction mechanism exists in the low temperature region whereas in high temperature zone, the material exhibits grain boundary scattering limited conduction. The composition dependent electrical conductivity is shown in Figure 7. It is seen that, initially, the conductivity increased upto $x = 0.05$ and then remained more or less the same for further increase in Hg-content in CdSe. This conductivity modulation can be correlated, at this stage, to a substantial decrease in an optical energy gap and partially to the improvement in the crystal structure.

The thermo EMFs generated by all the samples were measured in the 300–500 K temperature range. The samples are of the n-type conduction. From the experimental observations, it appeared that the temperature dependence of thermo power is approximately linear in the low temperature region whereas it deviates from the linear behaviour at higher temperatures. This is shown in Figure 8. The non-linearity of the plots indicates non-degeneracy of the material whose thermoelectric power is proportional to n^{th} power of the absolute temperature. As regards the film composition dependence of thermoelectric power, it decreases continuously with x . The carrier density n and carrier mobility (μ) were calculated from these studies for all the film structures. It has been observed that the mobility is a strong function of film composition and temperature whereas these variations are poor for the carrier density.

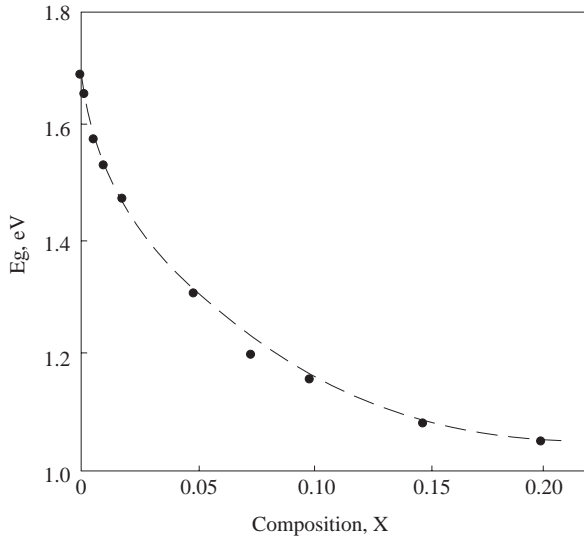


Figure 6. Variation of an optical gap Eg with the composition parameter x

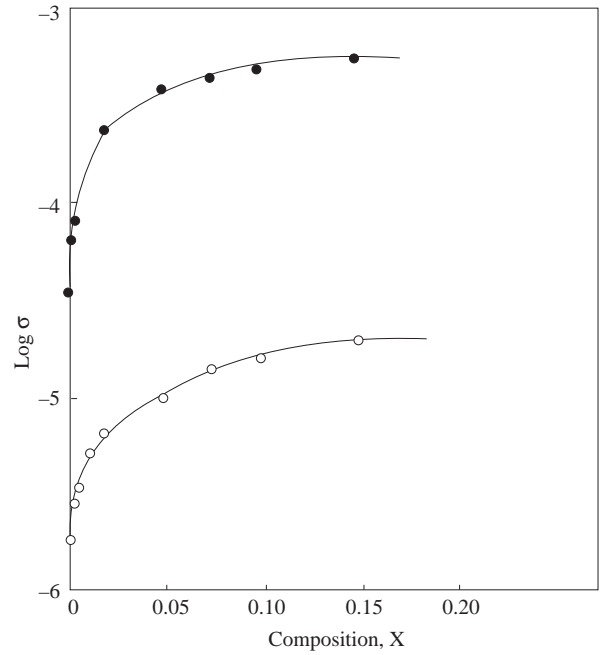


Figure 7. Dependence of $\log\sigma$ on Hg -concentration in the CdSe films at $T = 298$ K (\circ) and $T= 398$ K (\bullet).

The influence due to the film composition and temperature on the mobility and carrier concentration is shown in Figure 9. These variations also support the conductivity modulation. The intergrain barrier potentials were therefore, determined from the variation of $\log\mu T^{1/2}$ versus $1/T$ for all the samples and these values are listed in Table 1. It is seen that the intergrain barrier potential, ϕ_B decreased continuously with increase in Hg -content in CdSe.

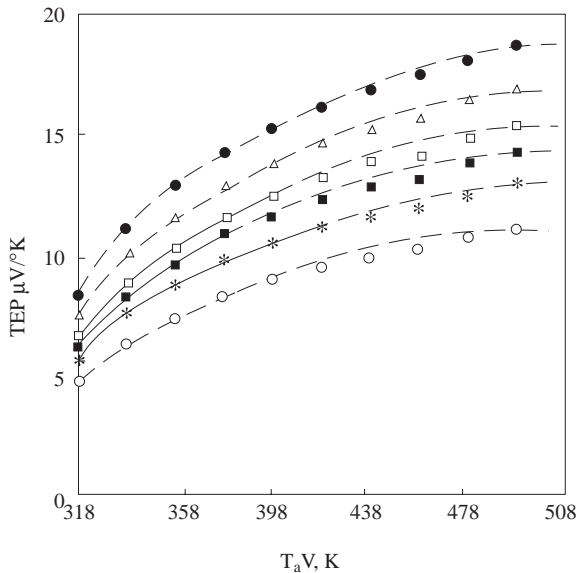


Figure 8. Temperature variation of thermo power for various x values: [$x = 0$ (\bullet), $x = 0.005$ (Δ), $x = 0.01$ (\square), $x = 0.02$ (\blacksquare), $x = 0.05$ ($*$) and $x = 0.10$ (\circ)

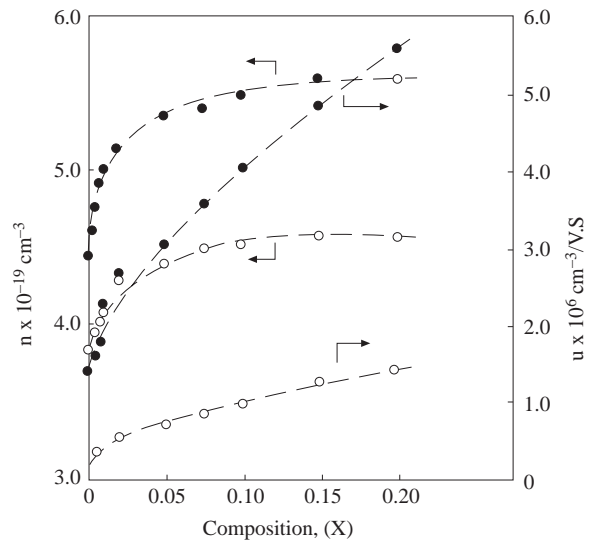


Figure 9. Dependence of carrier concentration n and mobility μ on composition parameter, x for $T = 418$ K (\circ) and $T = 478$ K (\bullet)

4. Conclusions

Following are the salient features of our studies.

1. The preparation procedure is employed for the first time to deposit $\text{Hg}_x\text{Cd}_{1-x}\text{Se}$ alloyed / mixed films and in general, is capable of producing good quality deposits of II-VI, IV-VI, III-V, I-III-VI binary / ternary materials of controlled variable compositions.
2. The deposition conditions and preparation parameters can easily be optimized to yield quality deposits. In our case the deposits obtained are thin, uniform, mechanically hard, adherent, pin-hole free and diffusely reflecting.
3. As regards the (Cd, Hg) Se films, the layer thickness went on decreasing with an increasing Hg-content in CdSe.
4. The compositional analysis showed that about 74% of the both materials get deposited on the substrate surface and variation of x_{film} with x_{bath} is nonlinear.
5. As-deposited (Cd, Hg)Se films are polycrystalline composed of the hexagonal wurtzite (dominant) and cubic zinc blend structures. The lattice parameters show nonlinear weak variation with the added Hg-content x in CdSe.
6. The optical absorbance measurements showed a high absorption coefficient with allowed direct type of transitions. The optical gap decreased, continuously with increased Hg-content in CdSe.
7. The electrical conductivity is found to be enhanced with the addition of Hg in host CdSe and the samples exhibit grain boundary scattering limited and a variable range hopping conduction mechanisms. The samples are of the n-type conductivity and the carrier density and mobility are both temperature and film composition dependent.

Acknowledgements

One of the author (VBP) is thankful to the University Grants Commission, Govt. of India, New Delhi for awarding fellowship under the faculty improvement programme (FIP) and to the authorities of Rayat Shikshan Sanstha and the Principal, Modern College, Vashi, Navi- Mumbai, for their kind permission to avail the fellowship.

References

- [1] N. C. Sharma , D. K. Pandya and K. L. Chopra, *Thin Solid Films*, **59**, (1979), 157.
- [2] J. F. Mc Cann, R. C. Kainthla and M. Kazacos -Skylas, *Sol Energy Mater*, **9**, (1983), 24.
- [3] S. H. Shin and J. G. Pasko, *Appl. Phys. Lett.*, **44**, (1984), 423.
- [4] Heribert Wiedemeir and A. E. Uzrpurvis, *J. Electrochem Soc.*, **130**, (1981), 252.
- [5] D. L. Smith, D. K. Arch, R. A. Wood and M. W. Scott, *Appl. Phys. Lett.*, **45**, (1984), 83.
- [6] L. P. Deshmukh and S. G. Holikatti, *J. Phys. D: Appl. Phys.*, **27**, (1994), 1786.
- [7] L. P. Deshmukh, C. B. Rotti, and K. M. Garadkar, *Indian J. Pure and Appl. Phys.*, **34**, (1996), 893.
- [8] G. S. Shahane, B. M. More, C. B. Rotti and L. P. Deshmukh, *Mat. Chem. Phys.*, **47**, (1997), 263.
- [9] D. Bhattacharya, S. Choudhuri, A. K. Pal, *Vacuum*, **43**, (1992), 313.
- [10] G. Micocci, A. Tepore, R. Rella and P. Siciliano, *Phys. Status Solidi (a)*; **148**, (1995), 431
- [11] R. L. Petritz, *Phys. Rev.*, **104**, (1956), 1508.