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Compositional effect on optical characteristic of solution grown $Cd_{1-x}Mn_xSe$ thin films

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The $Cd_{1-x}Mn_xSe$ thin films were grown from elemental selenium, sodium sulphite, cadmium chloride and $MnCl_2$, onto glass substrates by a solution growth technique. As-deposited films were annealed at 600 K. The optical absorption of annealed $Cd_{1-x}Mn_xSe$ thin films with different values of composition parameter x was then studied in the energy range from 1.10 to 4.0 eV. The $Cd_{0.5}Mn_{0.5}Se$ film showed allowed direct optical band gap with a room temperature gap of 1.58 ± 0.01 eV. Another direct transition observed in these films with x = 0.2, 0.3, 0.7 and 0.9 is ascribed to an optical transition from the crystal field split, valence band to the conduction band minimum. A third direct allowed transition from the spin-orbit valence band to the conduction band is also observed in x = 0.2, 0.3, 0.7 and 0.9 films.

1 Introduction

The n-type CdSe (band gap = 1.70 eV) and MnSe (band gap = 1.24 eV) semiconductors are becoming quite interesting and important[1-3] because of their major contribution in the solar cells, photodetectors, opto-electronics, light amplifiers, electrophotography, light emitting diodes, lasers photo- electrochemical cells and in the preparation of electronic elements based on the existence of metal insulator semiconductor (MIS) structures. Most of the research done so far has focussed extensively on determining the major features such as structural, optical and electrical properties of $Cd_{1-x}Mn_xSe$ compound in both single crystal and thin film forms. However, the study of influence of composition on opto-electronic characteristics of solution grown $Cd_{1-x}Mn_xSe$ thin films is rare in the literature.

The present paper describes a solution growth technique for the deposition of $Cd_{1-x}Mn_xSe$ films and systematic study of their optical properties[4] with the composition x. The technique is very simple, commercially viable and yields reproducible and more consistent results than the other sophisticated techniques[5-10].

2 Experimental Details

A series of $Cd_{1-x}Mn_xSe$ films with x = 0.9 were deposited by using a solution growth technique. The reaction bath contained solution of Na_2SeSO_3, MN^{2+} and $Cd(NH_3)_4^{2+}$. The solution composition was adjusted to achieve the desired stoichiometry for each $Cd_{1-x}Mn_xSe$ film. The process involves the reaction of Mn^{2+} and Cd^{2+} ions with Se^{2-} ions in a deionized water. An elemental selenium (99.95%) was dissolved in an aqueous solution of a sodium sulphite (pH > 9) at 363 K to form a partially unstable Na_2SeSo_3. The solution was then mixed with the tetra-ammonium salt of cadmium and aqueous solution of $MnCl_2$. In the solution state, unstable Na_2SeSO_3 yields Se^{2-} ions and forms the $Cd_{1-x}Mn_xSe$ compound. By maintaining the pH value at 9.4 and temperature at 323 K and varying the Cd/Mn ratio in the solution, uniform films of $Cd_{1-x}Mn_xSe$ are obtained in a duration of about 12 hr. Before using the substrates, they were cleaned with chromic acid and then with acetone to remove the substrate impurities and contamination if any and finally rinsed with deionized water and dried. The following chemical reactions are proposed.

$$Se + Na_2SO_3 \xrightarrow[12\ hr]{363\ K,\ ph = 9} Na_2SeSO_3\ \text{(partially unstable)} \quad ...(1)$$

$$CdCl_2 + 4\,(NH_3) \xrightarrow{300K} Cd(NH_3)_4Cl_2 \quad ...(2)$$

$$Na_2SeSO_3 + (1-x)\,Cd(NH_3)_4Cl_2 + xMnCl_2\ \text{(aqueous)} \longrightarrow Cd_{1-x}Mn_xSe\ \text{(film)} + \text{byproduct} \quad ...(3)$$

As-grown films were washed, dried and then annealed up to 600 K for 30 min with a regular interval to obtain reproducible results. The optical properties of the films were determined from the transmittance spectra obtained by employing a Hitachi-330 spectrophotometer. The film composition was determined by EDAX analysis. The thickness of the films was measured by Tolansky's method.

3 Results and Discussion

Table 1 shows a comparison between an initial and final composition of Cd, Mn and Se in the solution and in the film, respectively for seven different values of x. No appreciable change from starting stoichiometric ratio was observed in these films.

Fig. 1 is a representative case for x = 0.1, 0.5 and 0.7 which shows the transmittance spectra of these films deposited at 323 K and annealed at 600 K in air for 30 min. The values of the optical absorption coefficient are of the order of 10^4 cm^{-1} for near edge absorption given by

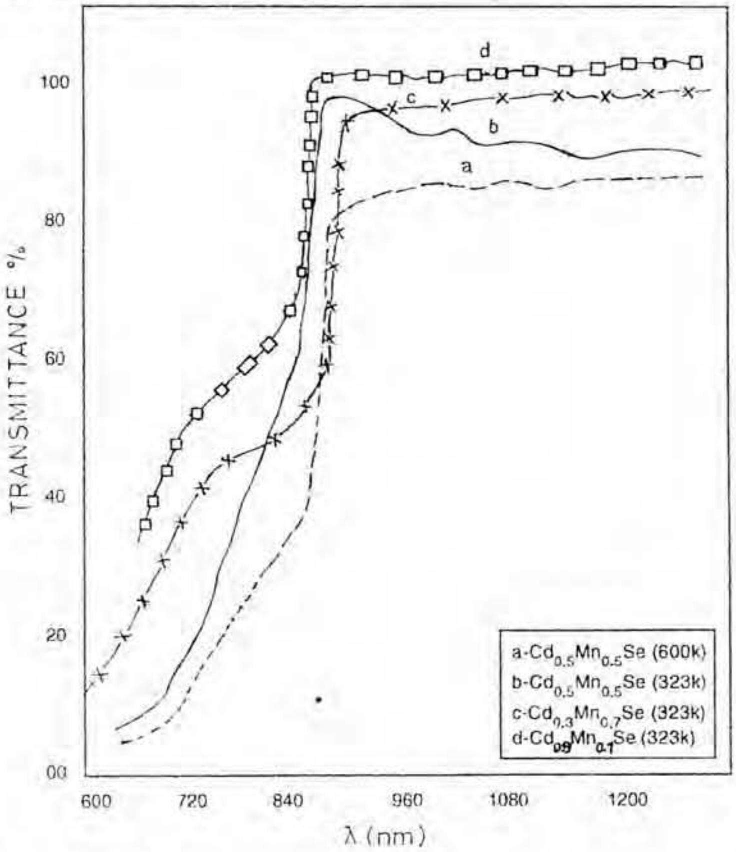

Fig. 1 — Transmittance T% versus wavelength (nm) for x = 0.1, 0.5 and 0.7 as deposited and annealed films

Table 1 — Comparison of results for $Cd_{1-x}Mn_xSe$ films annealed in air at 600 K for 30 min

Sr No	Composition X	Initial Composition in Solution	Atomic % (EDAX)	Final composition in Film
		Cd : Mn : Se	Cd : Mn : Se	Cd : Mn : Se
1	0.1	0.9 : 0.1 : 1.0	44.55 : 05.45 : 50.00	0.89 : 0.77 : 1.0
2	0.2	0.8 : 0.2 : 1.0	40.12 : 09.88 : 49.99	0.80 : 0.20 : 1.0
3	0.3	0.7 : 0.3 : 1.0	35.00 : 15.00 : 50.00	0.70 : 0.30 : 1.0
4	0.4	0.6 : 0.4 : 1.0	30.00 : 20.00 : 49.99	0.60 : 0.40 : 1.0
5	0.5	0.5 : 0.5 : 1.0	25.00 : 25.00 : 50.00	0.50 : 0.50 : 1.0
6	0.6	0.3 : 0.7 : 1.0	15.00 : 35.00 : 50.00	0.30 : 0.70 : 1.0
7	0.9	0.1 : 0.9 : 1.0	05.44 : 44.56 : 50.00	0.10 : 0.90 : 1.0

$$\alpha = -\frac{\ln T}{t} \qquad ...(5)$$

where, t is the thickness of the film. The values of α have been calculated, at different wavelengths, from these spectra using Eq. (6).

The plots of α versus $h\nu$ for three typical representative samples (x = 0.1, 0.5 and 0.7) are shown in Fig. 2. Such type of curves were also obtained for films with composition x = 0.2, 0.3, 0.6 and 0.9, in the photon energy range from 1.41 eV to 1.46 eV. The absorption coefficient, say α_1 for $Cd_{0.5}Mn_{0.5}Se$ obeys the relation

$$\alpha_1 = \frac{A_1}{h}(h\nu - Eg_1)^{1/2} \qquad ...(6)$$

Values of Eg_1 are represented in Table 2 and the representative curve of $(\alpha_1 h\nu)^2$ versus $h\nu$ shown in Fig. 3. The plots of $(\alpha_1 h\nu)^2$ versus $h\nu$ for $Cd_{0.3}Mn_{0.7}Se$, $Cd_{0.5}Mn_{0.5}Se$ and $Cd_{0.7}Mn_{0.3}Se$ compositions are also shown for comparison. This is due to allowed direct transition from the top of the valence band to the conduction band minimum at the center of Brillouin zone[7].

Table 2 — Technological parameters, composition and optical properties of $Cd_{1-x}Mn_xSe$ films annealed in air

Composition x	Thickness t (m)	Optical Band gap Eg_1 (eV)	Optical Band gap Eg_2 (eV)	Absorption Coefficient (cm^{-1}) $\alpha \times 10^4$
0.0	2.00	1.72	–	0.43
0.1	2.00	1.68	1.55	0.45
0.2	2.10	1.62	1.50	0.48
0.3	2.13	1.58	1.42	0.53
0.4	2.15	1.52	1.38	0.58
0.5	2.20	1.38	–	0.65
0.6	2.15	1.35	1.36	0.62
0.7	2.14	1.30	1.35	0.59
0.8	2.20	1.23	1.32	0.55
0.9	2.16	1.16	1.30	0.52

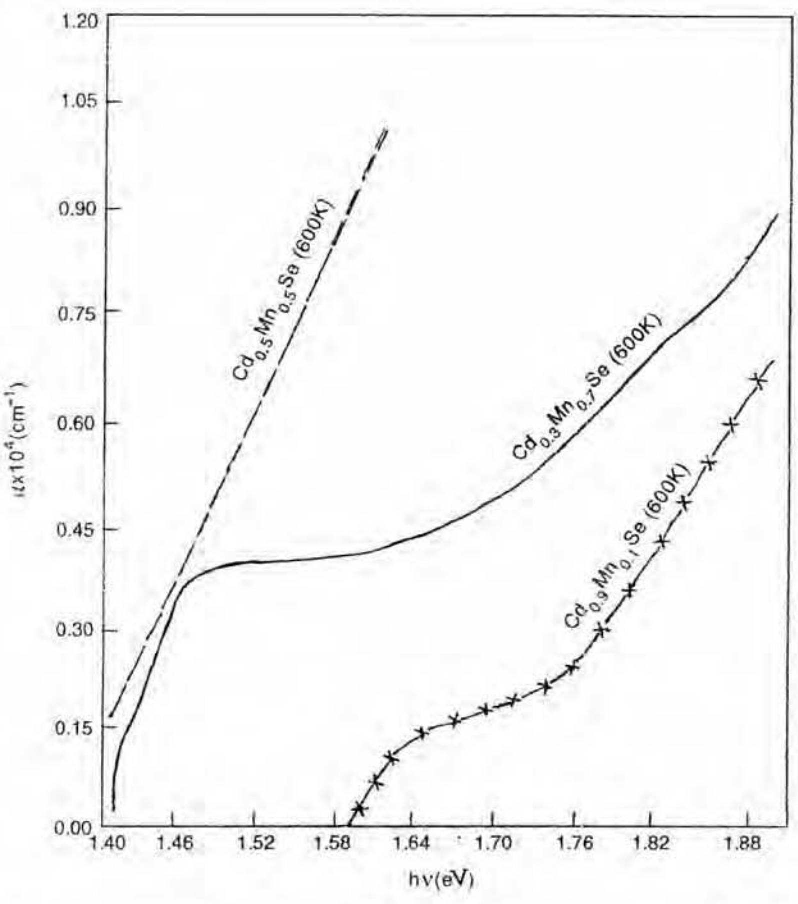

Fig. 2 — Absorption coefficient (cm^{-1}) versus $h\nu$ for x = 0.1, 0.5 and 0.7 annealed films

If α_1 is calculated using the value of A_1 and Eg_1 obtained from Eq. (6) by a least squares fit, it is found that α_1 is lower than the observed value at energies $h\nu > 1.46$ eV. This deviation is due to the onset of an additional absorption process.

Similarly, analysis of $\alpha_2 = \alpha - \alpha_1$ in the energy range 1.49-1.70 eV shows that α_2 follows the relation

$$\alpha_2 = \frac{A_2}{h}(h\nu - Eg_2)^{3/2} \quad ...(7)$$

with Eg_2 given in Table 2. Representative plots of $(\alpha_2 h\nu)^{2/3}$ versus $h\nu$ are shown in Fig. 4 for $Cd_{0.3}Mn_{0.7}Se$ and $Cd_{0.7}Mn_{0.3}Se$ film compositions. This is due to a transition from the crystal-field-split valence band to the conduction band minimum[11]. At energies, $h\nu > 1.70$ eV, α_2 once again deviates from the observed values shown in Fig. 2. Obviously, this is due to transition from the spin-orbit valence band to the conduction band.

From Table 2 it is seen that X variation causes a regular decrease in direct allowed optical band gap Eg_1 from 1.72 eV to 1.12 eV as X is varied from 0 to 0.9. Further it can be seen from Table 2 that forbidden direct band gap Eg_2 also decreased with increase in X value in $Cd_{1-x}Mn_xSe$ films. The excess Mn in the lattice makes the donor levels degenerate and merge into the conduction band of $Cd_{1-x}Mn_xSe$, thus decreasing the optical band gaps, Eg_1 and Eg_2. For the composition $Cd_{0.5}Mn_{0.5}Se$ as only allowed direct optical band gap (Fig. 2), it may be suggested that this deviation is due to the transformation of crystal structure from cubic (x = 0.1 to 0.4) to hexagonal tetragonal (x = 0.5 to 0.9)[12].

The absorption coefficient α also changes with the respective x value presented in Table 2. It is therefore suggested that $Cd_{1-x}Mn_xSe$ thin films will be of use in photovoltaic device applications.

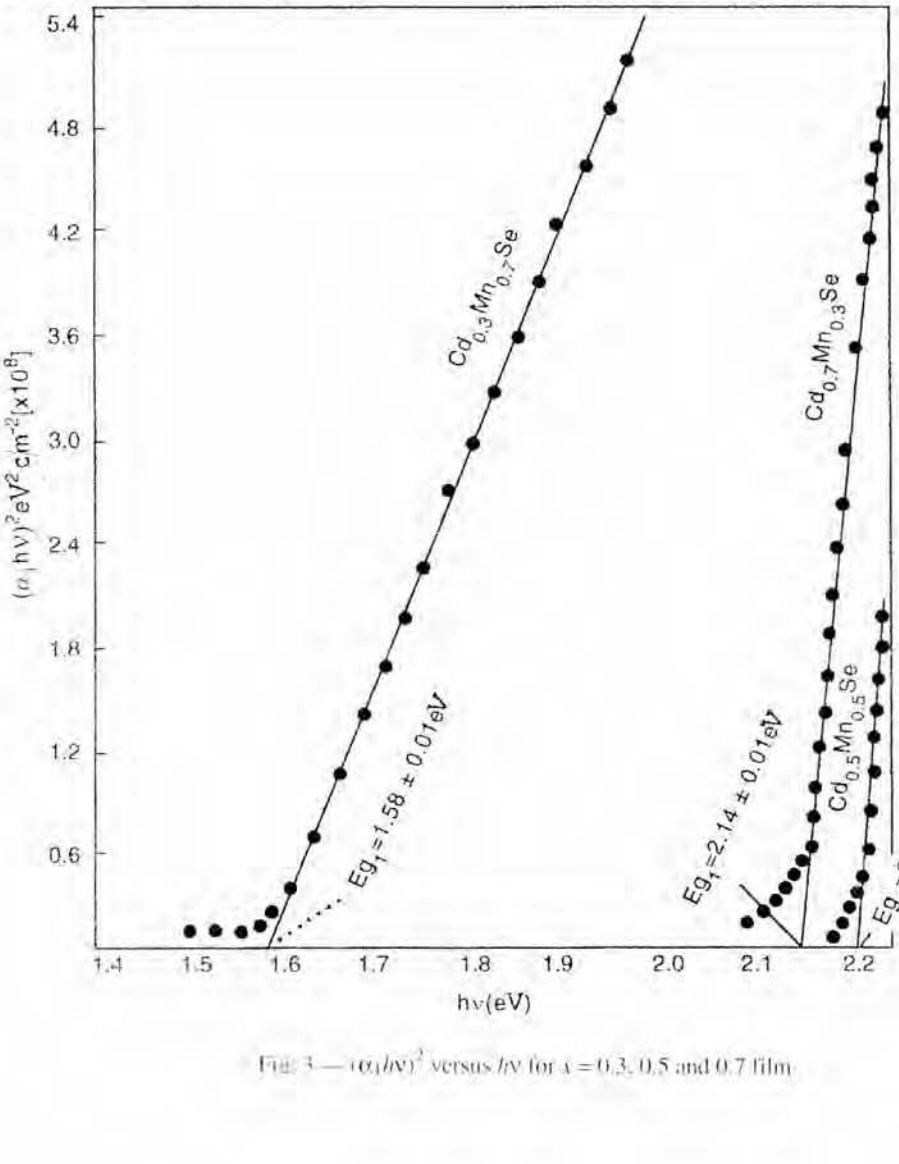

Fig. 3 — $(\alpha_1 h\nu)^2$ versus $h\nu$ for x = 0.3, 0.5 and 0.7 film

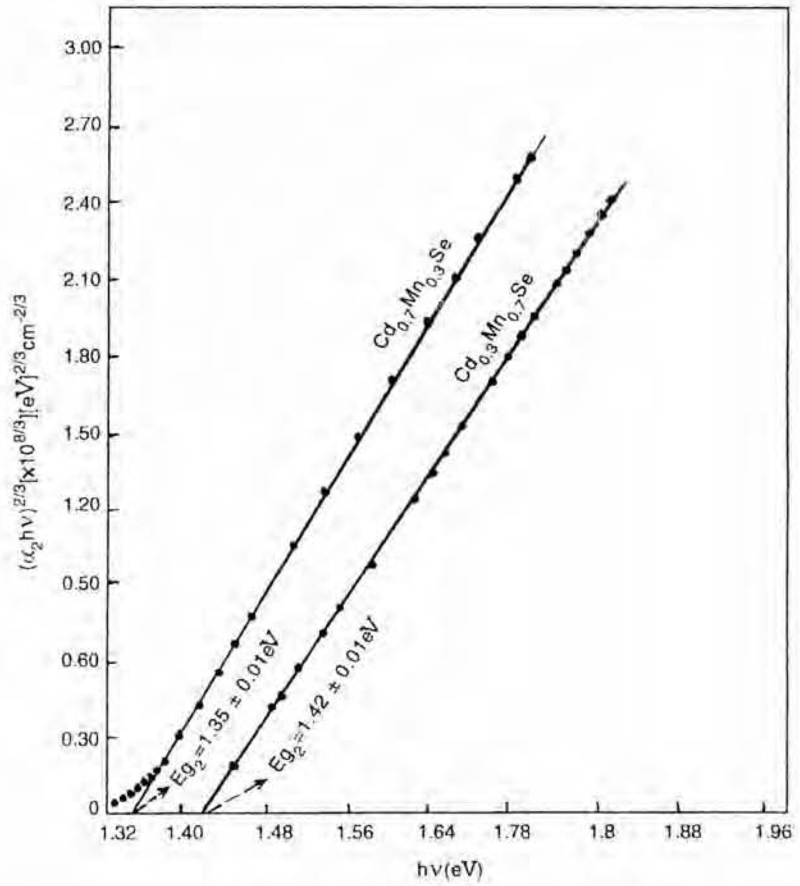

Fig. 4 — $(\alpha_1 h\nu)^{2/3}$ versus $h\nu$ for $x = 0.3, 0.7$ film

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