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Poole -Frenkel Photoconductivity in Synthesized Cdse: Mn^{+2} Ions Thin Films

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Abstract
CdSe semiconductors were synthesized with Mn^{+2} odd dopants from 1-9at.% onto ultrafine ITO glass substrates. Successive Ionic layer Adsorption and reaction (SILAR) technique was used in the synthesis. With proper fabrication of metal electrode contacts and 5mm inter electrode spacing across the films, photoconductivity was measured with a high input impedence (10^{14} Ω) electrometer amplifier under -108V-0-(+108)V in both polarity of applied bias and was found to obey two distinct conduction mechanisms – ohmic in low field and Poole - Frenkel type at high fields within the regions of the applied fields.

Keywords: CdSe, dopants, SILAR, photoconductivity, Poole - Frenkel effect

1. Introduction:

Cadmium Selenide semiconductor compound belongs to II-VI binary compound semiconductors of cadmium and selenium having hexagonal, cubic or mixed crystal structure. CdSe is highly photosensitive material due to its energy band gap 1.74eV which matches the maximum intensity in the visible range of the solar spectrum in two solar spectral phases -(a) thermal part with $h\nu<E_g$ and (b) optical par with $h\nu>E_g$[1,2]. CdSe thin film polymer nano-composites find potential technological applications in fabrication of devices like photovoltaic cells, thin film field effect transistors, light emitting diodes, optoelectronic devices and other nanoscale devices [3-5]. Unlike the bulk CdSe compound, nanosized CdSe attracts more attention of scientists and researchers on its exciting characteristics to be used as window layer in photovoltaic cells[6] . Besides, polymerized nano-composites thin films find versatile functions to display enhanced optical, opto-electronic, mechanical and magnetic properties[7]. In this paper, we investigate and report the Poole-Frenkel photoconductivity in chemically synthesized CdSe doped Mn^{+2} – ions thin films and further results will be highlighted in the next publications.

2. Materials and Method :

Successive Ionic Layer Adsorptionand Reaction (SILAR) technique was used for synthesis of PVA matrixed equimolar CdSe : Mn^{+2} nanocomposite thin films. In the process, high purity (99.99%) (**AR grade –Aldrish Sigma**) $CdCl_2$ was used as Cd^{+2}-cation source and freshly prepared sodium selenosulphate (Na_2SeSO_3) as Se^{-2}-anion source in presence of trisodium citrate ($Na_3C_6H_5O_7$) as reducing agent. Pure ammonium hydroxide (NH_4OH) was used to adjust the pH of the precursor

solution. Polyvinyl alcohol (PVA) matrix was used for controlling the growth and stabilisation of surface morphology of the CdSe thin films. Pure manganese chloride ($MnCl_2$) was used as doping material in the synthesis work at concentrations (1, 3, 5, 7, 9) at. %.

In the process, we prepared 0.4M $CdCl_2$solution by dissolving 8.053 gm of $CdCl_2$ in 100ml de -ionized water. We also prepared 2wt.% PVA solution by dissolving 2gm of PVA in 100ml de-ionized water and the resultant solution was refluxed for 30mins with constant stirring. Now 50ml of $CdCl_2$ solution was mixed with 50ml of PVA solution in a 200ml beaker. Now we prepared 1 at.% Mn^{+2} solution by dissolving 0.071gm of $MnCl_2$ in 5ml DI water. The two precursor solutions were mixed and the entire mixture was stirred for 5mins. The properly cleaned ITO glass substrates (4nos.)were fully immersed vertically in the precursor solution for 8hrs when Cd^{+2}-ions were adsorbed. The substrates were removed and stabilized for 10mins and then gently rinsed with DI water for removal of loose Cd^{+2} –ions.

Preparation of 0.4M sodium solenosulphate (Na_2SeSO_3) solution:

We dissolve 5.04gm of sodium sulphite (Na_2SO_3) at 0.4M in 100ml DI water. Then 0.05mole powder selenium was added to the precursor solution and the resultant mixture was refluxed at 70^0C for 1hr with constant stirring when we obtained 0.4M sodium solenosulphate (Na_2SeSO_3) solution.

Now the substrates were immersed into the precursor solution mixed with 10ml of trisodium citrate and a few drops of NH_4OH solution at pH = 8 for 8hrs when Se^{-2}-ions were adsorbed on the Cd^{+2}-ions pre-deposited substrates. The two opposite ions Cd^{+2} and Se^{-2} –ions reacted to form CdSe doped Mn^{+2} –ions at 1 at.% at 0.4M. The substrates were gently removed, stabilized, rinsed in running DI water, dried in an oven and finally annealed at 50^0C for 24hrs. Similarly we synthesised CdSe thin films doped with Mn^{+2} at doses 3, 5, 7, 9 at.% at 0.4M.

Highly pure photograde silver electrodes were deposited on the CdSe doped films with electrode separation of 5mm to obtain Ag/CdSe/Ag cell configuration with the help of Hind High Vacuum Coating Unit under vacuum pressure ~1.33×10^{-4}Pa for which Ta-boats were used as the source heater. The surface area of the films between the electrodes were ~$10 \times 5mm^2$. The sample films were successively suspended vertically with thin enamelled copper wires inside a glass jacket evacuated continuously with the help of double stage rotary pump to a pressure ~ 2.67Pa. The sample was illuminated uniformly with white light obtained from a tungsten halogen lamp (250W) attached with a parabolic focussing mirror and the intensity of light was measured with the help of a sensitive APLAB luxmeter. High ambient temperatures inside the glass jacket were achieved with the help of a resistive heater connected with a power supply and measured with the help of a copper – constantan thermocouple coupled with a digital micro voltmeter. The dark current and the current under illumination were measured with the help of a high input impedence (~ $10^{14}\Omega$) electrometer amplifier under different applied bias. The whole experimental set-up was housed inside a suitably wooden grounded Faraday case to minimize the ground loop currents and noises.

3. Results and Discussion

Poole-Frenkel photoconductivity

The photocurrent density in the sample is defined as

$$J_{ph} = \frac{J-D}{D} \quad (1)$$

where J is the current density under illumination and D the corresponding dark current density. The variation of photocurrent density (J_{ph}) vs. slots applied bias (V_a) across the CdSe : 9at.% Mn^{+2} sample in the range -108V to +108V under different illumination intensity is shown in Figure 1. Two distinct photoconduction mechanisms at low and

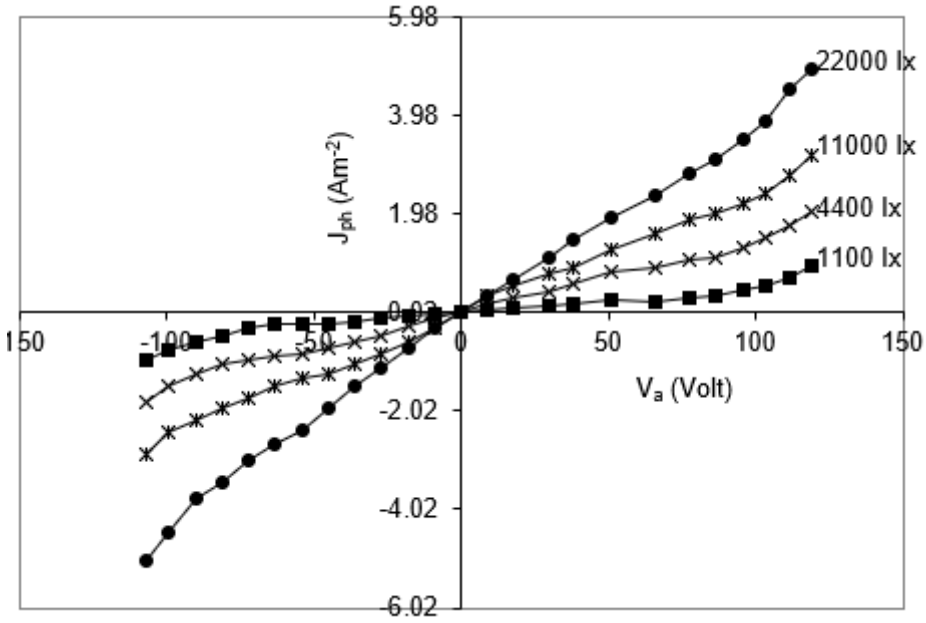

Fig.1. J_{ph} vs. V_a for CdSe : 9 at.% Mn^{+2} films illuminated with different intensities of white light.

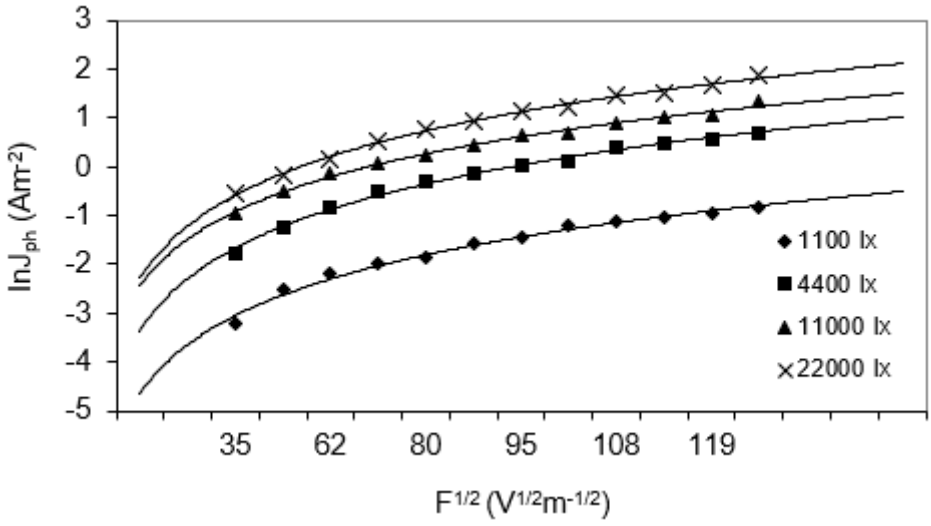

Fig. 2. InJ_{ph} vs. $F^{1/2}$ for CdSe :*9at.% Mn^{+2}* films illuminated with different intensities of white light.

high applied field regions are observed in the characteristics. At low voltage region upto 50V with respect to both polarity of applied biases, the characteristics are linear symmetrically about the origin and show that the photoconductivity in the low field regions are ohmic. The current density beyond the applied low voltage regions in both polarities, are found to increase nonlinearly with the appllied bias and establishes the non-ohmic characteristics. The study of In J_{ph} vs, $F^{1/2}$ of the host sample as shown in

Figure 2 where F is the field corresponding to the applied bias shows that the characteristics are found to be linear in the high field regions. This may be explained that in the high field regions, the high applied field reduces the grain boundary potential barriers (ϕ_b) and hence the current density increases exponentially [8], as can be seen from the relation,

$J = J_0 \exp(\beta_{pf} . F^{1/2/kT})$ (2)

where J_0 (= σF) is the low field current density, β_{pf}, the Poole-Frenkel co-efficient, k the Boltzmann constant and T the room temperature. This clearly shows that the conduction mechanism in the sample in the high field regions is of Poole-Frenkel type.

Again, in conformity with the plot of InJ_{ph} vs. $F^{1/2}$ as shown in Figure 2, the characteristics are found to be linear in the high field regions. The reason can be explained on the basis of the mobility activation process on account of barrier modulation in the host sample and the effective mobility of carriers is given by [9,10]

$\mu_{eff} = \mu_0 \exp(-q\phi_b/kT_0)$ (3)

where μ_0 is the carrier mobility without potential barrier, T_0 the characteristic temperature of the barrier modulation process. The evaluated values of Poole-Frenkel coefficients calculated from the slops of two identical films at CdSe-5 at.% and 9 at.% Mn^{+2} at the illuminating intensities of WL have been shown in Table-1.

Table- 1. Observed values of β_{PF} for CdSe doped films

CdSe doped films	Intensity 11x 10^2 (Ix)	Intensity 44x 10^2 (Ix)	Intensity 11 x 10^3 (Ix)	Intensity 22 x10^3 (Ix)
	β_{PF} ($eVm^{1/2}V^{-1/2}$)	β_{PF} ($eVm^{1/2}V^{-1/2}$)	β_{PF} ($eVm^{1/2}V^{-1/2}$)	β_{PF} ($eVm^{1/2}V^{-1/2}$)
5at.% Mn^{+2}	5.45 x 10^{-4}	6.75 x 10^{-4}	6.77 x 10^{-4}	7.19 x 10^{-4}
9at.%Mn^{+2}	5.12 x 10^{-4}	5.76 x 10^{-4}	6.27 x 10^{-4}	6.71 x 10^{-4}

As the intensity of illumination increases, the number of photogenerated carriers is also increased while some part of the photogenerated carriers contribute in reduction of the grain boundary potential barrier heights and other contribute to the photocurrent . The resultant effective current density in this type of Poole-Frenkel conductivity can be expressed as [9,10]

$J_{eff} = n_p q F \mu_0 \exp(\beta_{pf} . F^{1/2/kT} - q\phi_b/kT_0)$ (4)

where n_p is the majority photo-generated carrier density. The equation (4) co-relates the J_{eff} with the Poole-Frenkel effect and the barrier modulation due to illumination. The barrier modulation process in Jeff is a result of two contributions, one from the illumination and other from the applied bias.

3. Conclusion

The photoconductivity of the chemically synthesized Mn^{+2} –ions doped CdSe thin films using SILAR technique is found to be characterized by both Poole-Frenkel type and barrier modulated photoconductivity processes.

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