An Analysis Of Photocurrent Growth And Decay Characteristics In Chemically Synthesized Cds Nanocrystalline Thin Films.

M. Dinendra Singh And K. Kunjabali Singh*

Department Of Physics, Himalayan University, Itanagar-791111 , Arunachal Pradesh, India.
*Thin Films & Nanomaterials Research Laboratory
Department Of Physics, Thambal Marik (Govt.) College, Oinam-795134, Bishnupur District, India.

Abstract:
Nanocrystalline CdS thin films were synthesized on ultrafine cleaned micro glass substrates at different equimolar solutions $0.05M \leq 0.2M$ by Chemical Bath Deposition method.The p^H of the solution was adjusted at 10 during entire synthesis process. A gap-type Ag-CdS – Ag thin film cell configurations were fabricated with film-electrode ohmic spacing of 5mm and illuminated successively with white photon intensities under constant applied field inside continuously evacuated vacuum sealed glass jacket. Photocurrents were measured and analysed as function of time of illumination. The photocurrent rise and decay in the CdS thin films revealed various distributions of discrete traps and recombination centres in the band gap leading to production of excess carriers by some excitation process.
Key words *: Cadmium sulphide, CBD, photocurrent, traps.*

I. Introduction

Nanoscience and nanotechnology have become most fascinating field of research in all branches of material science, biological science and other branches of sciences world-wide during the last decades. Particles with diameter 1-100nm are called nanomaterials which may have varied structures like globular, rode-like, plate-like, flower-like, leaves-like or more complex structures. Spherical particles with size ‹10nm are called clusters or quantum dots. In nanoscale, diameter of materials is of the order of d-Broglei wavelength of the electron wavefunction.[1] Therefore, the electronic and optical properties of matter are changed and new properties are produced quite different from those of bulk materials.

Photoconductivity in a material is the manifestation of photo-electrical conductivity caused by interaction of light quanta with the material which results in the production of free mobile carriers on suitable absorption of quantum of energy.Under a suitable applied electric field, , a constant photocurrent is generated in the external circuit. This photo-electrical process finds several applications in electronic industry and research.[2] Cadmium Sulphide is one of the prominent family members of II-VI class of bulk compound semiconductors. With a direct band gap of 2.4eV, this compound semiconductor in thin film forms finds wide range of technological applications for successful fabrications of low cost high efficiency thin film solar cells,[3,4,5,6,7]laser diodes,[8] photochemical Cells,[9,10] X-ray detectors[11] and I R detectors.[12] A variety of physical and chemical routs for deposition and synthesis of CdS semiconducting thin films have been reported by a number of research workers during the last decades for achieving good quality thin films. Therefore, a systematic approach for selection of a method is necessary for synthesis and deposition of semiconducting thin films. In the present work, Chemical Bath Deposition (CBD) technique is used for synthesis of CdS nanocrystalline thin films relative to less time consumption and less economic.

II. Experimental Details

CdS nano-composite thin films were synthesized by CBD technique on ultra fine cleaned micro-glass slides at different equimolar (EM) solutions in the range $0.05M \leq x \leq 0.2M$. A R grade cadmium sulphate $(CdSO_4)$, thiourea,$(CS(NH_2)_2$ and ammonia (NH_3) solution were used. For 0.05M CdS thin films, we dissolved 3.8gm of $CdSO_4$ in 100 ml of De-ionized (DI) water and stirred uniformly for 15 min with a hot-plate electro-magnetic stirrer for homogeneity of the solution. Then, NH_3 solution was added drop-wise to the precursor till the solution turned into analkaline white turbid. Excess NH_3- solution was added till the solution became clear with the production of $Cd(NH_3)_4^{2+}$ ions in the solution. The p^H of the solution was adjusted at 10 using a digital p^H-meter. An EM solution of thiourea was prepared into 100ml of DI water at RT and then

stirred for 15 min. The precursor was then added to the alkaline precursor solution in the ratio 1:4 while the matrix was continued stirring for 1.30 hr at 70^0C and cooled down at RT. The chemically and ultrasonically cleaned substrates were immersed vertically into the reaction bath for 24 hr using a suitably designed substrate holder properly clamped. The substrates were removed from the bath when we obtained CdS thin films deposited, which were then kept for 30 min in a desiccator for stabilization, washed several time with running DI water after which were crystallized in an oven at 10^0C above RT for 30 min. Similarly, we synthesized CdS films of different molars x = 0.1M, 0.15M and 0.2M by dissolving appropriate amount of $CdSO_4$ and $Cs(NH_2)_2$ in DI water. The details structural and optical reports were published in earlier paper.[13]

A gap-type CdS film cell configurations and to ensure good ohmic contacts for photoconductivity measurements, a photo grade purity Ag electrodes of 4.0 x $10.0mm^2$ sizes were uniformly vacuum deposited over CdS thin films using properly designed mica-masks inside **HINDHIVAC 12 A** 4 vacuum Coating Unit under vacuum pressure 1.33 x 10^{-4}Pa to obtain Ag-CdS- Ag gap type cell configuration with inter-electrode spacing of 5mm. The samples were successfully mounted on a suitably designed sample mount which were then suspended vertically inside a continuously evacuated glass jacket using thin enamelled copper wires under low vacuum pressure ~ 2.67 Pa for which a double stage rotary pump was used. A suitably designed optical arrangement was made to illuminate the sample uniformly for a period of 30-40mins with a constant intensity of white light obtained from a tungsten halogen lamp (250W-24V) light source attached with a parabolic focussing mirror. An APLAB-Luxmeter (**model 5011S**) was used to measure the intensity of the incident light inside high ambient temperatures achieved using a resistive heater connected to a stabilized power supply. During the period of optical excitation, photocurrent (I_{ph}) started growing exponentially to reach the steady state, and the currents were recorded after an intervals of 5 mins. The light was cut –off using a mechanical shutter for the next 30mins when photocurrent started decay exponentially to reach the initial dark value. The dark currents and the currents under illumination were measured after an interval of   5 mins with the help of high input impedence (~10^{14} Ω) ECIL electrometer amplifier under different d.c. bias voltages.

III. Results And Discussions

3 (i) Effect of molarity on the growth and decay of photocurrent in CdS films
Photosensitivity of a material is an effective optical parameter in measuring photoconductivity defined as

$$S = (I_L - I_D)/I_D = I_{ph} / I_D \qquad (1)$$

where $I_{ph} = (I_L - I_D)$ is the photocurrent, I_L the current under illumination and I_D the dark current. The variation of photocurrent growth and decay as a function of time of illumination under different intensities of WL of CdS thin films at molars x = 0.05M, 0.10M, and 0.15M have been shown in Figs (1,2 & 3).
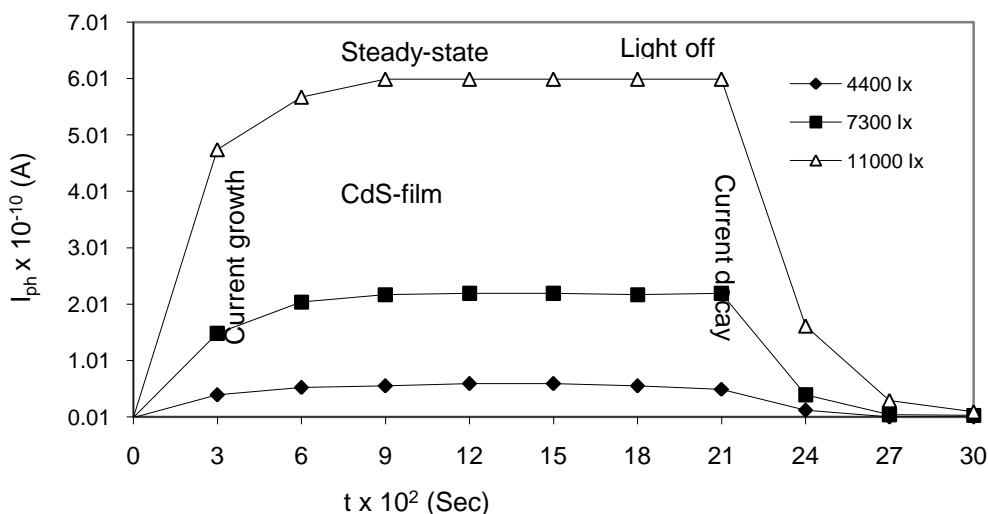

Fig.1. Growth and decay of photocurrent with time in 0.05M CdS films **.**

On exposition to external illumination of WL with sufficient photon energy $h\gamma \geq E_g$, photocurrent increases exponentially to reach the maximum steady state within some fractions of a second. The time interval to reach the steady state is growth time (T_g). In this process, new carriers are generated accompanied by their recombination. Photocurrent, therefore, requires some time to grow and reach the maximum value. As the density of excess carriers increases, the recombination rate between carriers (electrons and holes) is also enhanced. However, after a lapse of time from the start of illumination of the sample, concentration of electron-hole reach equilibrium and is maintained as long as photon excitation remains unchanged. The photoconductivity in this situation is known as steady state photoconductivity.[14,15] Once the steady state is maintained, there must be electron-hole recombination at the same rate at which they were generated, under which the concentration of electrons and holes attain some constant value. If the excitation light is turned off, the excess carriers recombine thereby decreasing the free life time which results decreasing in photoconductivity exponentially to reach the initial dark value within some finite time called decay time (T_d) .

3.(ii) Effect of molarity on trap depths in CdS films
        Further, the study of growth and decay characteristics of photoconductivity in the CdS thin films reveals the presence of various electron-hole trap distributions, trapping levels, trap cross-sections etc. within the forbidden energy gap.
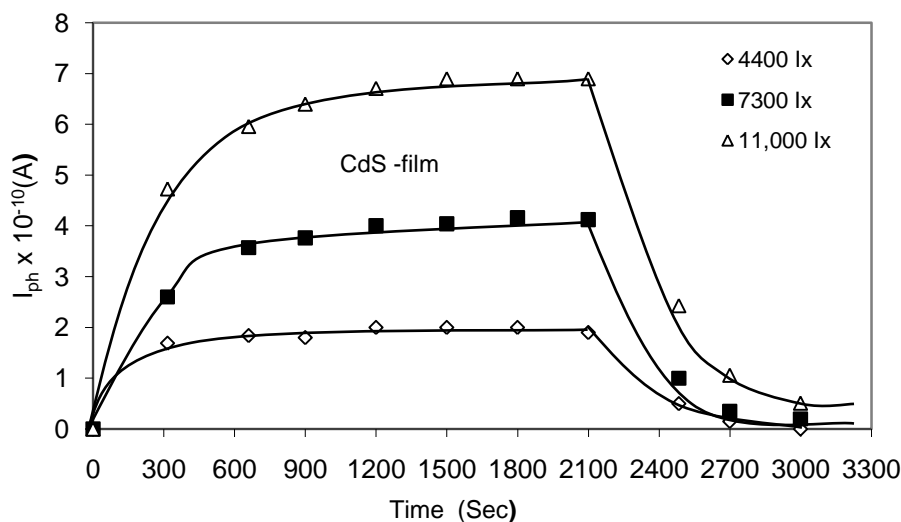

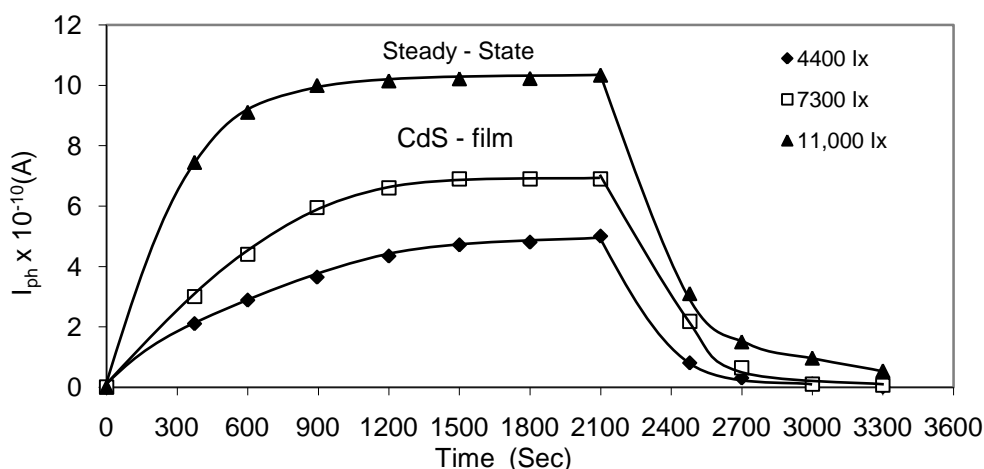Fig.2. Photocurrent growth and decay vs. time 0.10M CdS films.

Fig.3. Photocurrent Growth and decay vs.time in 0.15M CdS films.

Table-1. Photocurrent growth and decay time in CdS films at different levels of illumination.

Induced molarity (M)	Thickness (Å)	Applied bias (36V)		
		Intensity (lx)	T_g (min)	T_d (min)
0.05	1500	4400	10	2.50
		7300	5.0	1.67
0.10	2000	11000	5.0	1.25
		4400	5.0	2.30
		7300	4.6	1.17
		11000	4.2	0.75
0.15	2500	4400	4.9	2.25
		7300	4.5	0.83
		11000	4.1	0.50

Table-2. Discrete trap depths in CdS nanocrystalline thin films.

Induced molar (M)	Trap-depths under levels of WL illumination		
	4400 lx	7300 lx	11000 lx
0.05	0.75	0.74	0.73
0.10	0.74	0.75	0.74
0.15	0.76	0.74	0.75
0.20	0.75	0.76	0.73
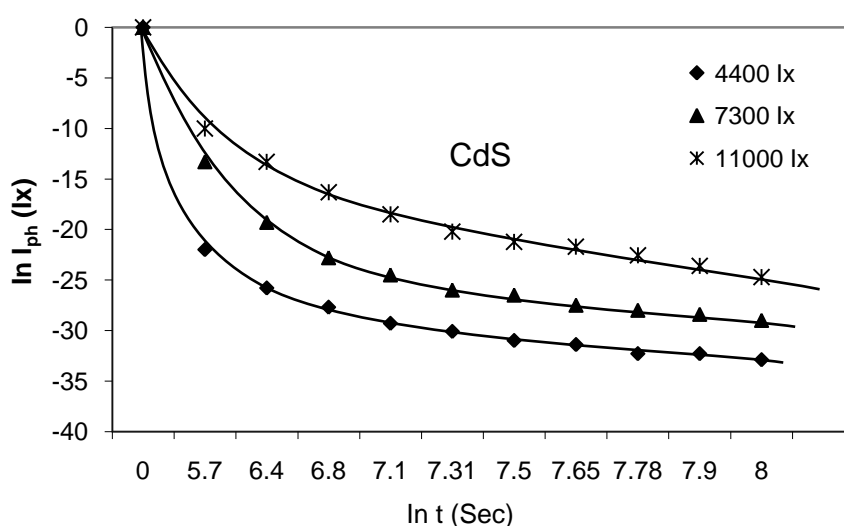
Fig. 4. In I_{ph} vs. In t of a CdS nanocrystal film, (2500Å) illuminated with different WL intensity,Va=36V.

The sub-linear behaviour of the characteristics shows the inter-relationship between traps and recombination centres in the films. Table -1 shows the observed values of growth time (τ_r) and decay time (τ_d) of the films at different induced molars and intensities of illumination. It is observed that in each set of the films a decrease in τ_r and τ_d with increasing intensity of illumination resulted. This is expected that the number of free carriers is much greater than the number of trapped carriers, and hence electrons recombine with holes

without significantly involving the trapping process.[16] The values of τ_r and τ_d for the films are also found to decrease with increasing molars, and the decay times for each intensity of illumination of the film is less than the corresponding growth times of photocurrent.

Further, the traps which have been filled during the excitation of the material will be emptied when the excitation is removed at a rate depending on their capture cross-section and their ionization energies. If re-trapping of carriers from traps is negligible, then exponential decay is expected.

The trap depth E in the energy gap can be calculated using the relation,[17]

$$E = kT[\ In S - In\ \frac{In(I_o/I_t)}{t}\ ] \qquad (2)$$

where I_0 is the photocurrent at t=0, I_t the photocurrent at time t after switching on light, S the frequency factor equal to 10^{10} per second, k the Boltzman constant and T the room temperature. The values of trap depths at different molars and levels of excitation in CdS nanocrystallient films were calculated from the exponential photocurrent decay curves and have been are shown in Table-2. The estimated values of observed trap depths are found in the range $(0.73 - 0.75)eV$

IV. Conclusion

Molar dependent photocurrent growth and decay times in chemically synthesized CdS thin films are observed dependent on concentrations of Cd^{+2} and S^{-2} ions, applied bias and intensities of excitation radiation. The growth and decay times of photocurrents are observes decreasing with increase of molars and intensity of illumination. Various traps and recombination of carriers are observed in discrete trap levels.

Acknowledgements

References

[1]. Email Roduner, Nanoscopic Materials-Size Dependent Phenomena, Institute Of Physical Chemistry, University Of Stuttgari, Stuttgari, Germany, The Royal Society Of Chemistry, 2006.
[2]. Nikhil Rastrogi, Manish Serma, Awmesh Agarwal, R . K. Agarwal, Shiv Singh, Acta Ciencia, Vol.   Xxviii, 065(2002)
[3]. K. Kunjabali Singh, Manoranjan Kar, And H. L. Das, Indian Journal Of Pure & Applied Physics, Vol. 48, Feb., 2010, Pp 110-114.
[4]. Panda S K, Chakrabarti S, Satapti B, Satyam P V And Choudhuri S, J Phys D Appl Phys., 37(2004)   628.
[5]. Rincon M E, Martinez M W And Miranda-Hernandez M, Thin Solid Films, 425(2003) 127.
[6]. Balakrishnan K S And Rastogi A C, Thin Solid Films, 163 (1988) 279.
[7]. Entinu G, Squillante M R, Serreze H B And Clarke E, Ieee Transnucl Sci, 28(1981) 558.
[8]. Panda Sk, Chakrabarti S, Satpati B, Satyam Pv And Choudhuri S, J. Phys, D Appl. Phys,   37(2004)628.
[9]. Rincon Me, Martiz Mw And Mivande-=Veruandez M, Thin Solid Films, 425(2003)127.
[10]. Balakrishnan Ks, And Rastogi Ac, Thin Solid Films, 163(1988)279.
[11]. Elinu G, Squillante M R, Serreze Hb And Clerke E, Ieee Trans Nucl Sci, 28(1981)558.
[12]. Fauri J And Millan Am, J Of Crst Growth, 54(1981)582.
[13]. M Dinendra Singh And K Kunjabali Singh, Iosr Journal Of Applied Physics (Iosr-Jap) Ɛ-Issn : 2278-4861 Vol. 8, Issue 5 Ver Iii (Sep-Oct, 2016), Pp 70-75.
[14]. Z Paroda And E Schaboroska, Thin Solid Films, 66(1980)L55.
[15]. S M Ryvkin, Photoelectric Effects In Semiconductors, Consultants Bureau Enterprises, Inc. (1964), New York Chap. Ii, P-19.
[16]. M. Buragohain And K. Barua, Indian J. Phys. 59a (1985) P: 178-184.
[17]. B.N. Srivastava And S. Sing, Indian Journal Of Pure & Applied Physics, 8(1970)Pp 716- 724.