Photoresponse properties of CdTe : Ce^{+3} synthesized nanocrystalline thin films

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Abstract:

Nanocrystalline CdTe matrix thin films implanted with Ce^{+3} ions at different doses were grown by SILAR technique onto ITO glass substrates at RT. The photoelectrical properties of the films were studied with constant illumination of white light of different intensity under d.c. applied bias in vacuum pressure ˙2.67Pa.The I-V characteristics of the films at Ce^{+3} at 2 at.% and 8 at.% revealed distinct linearity and symmetrical about zero applied bias which showed ohmic-film-electrode contacts, enhanced with Ce^{+3} ion concentrations. The photocurrent and photosensitivity in the films showed linear dependent on intensity of the illuminating white light, applied bias and the doping ion concentrations. Bimolecular recombination between carriers were observed predominating the photoconduction mechanism of the films. Such dependence of photocurrent and photosensitivity on intensity of illumination, bias and doping ion concentrations implies that the absorption coefficient of white light becomes higher and some physical parameters like electron - hole traps and donor or acceptor levels are uniformly distributed in the energy gap of the films. The nature of such dependence of photosensitivity in the films' parameters ` reveals the presence of large number of defect density.

Keywords: *CdTe thin films, SILAR, doping, photo-excitation, photosensitivity*

I.   Introduction

Photoconductivity phenomena in materials is the manifestation of interaction of light quanta with the solid material, resulting in the production of mobile charges by the absorption of radiation of suitable quantum of energy and enhances its electrical conductivity. Thus, photoconductivity process is based on absorption of photons and gives rise to free carriers which under suitable electric field, drift into the interior of the solid and generate constant electric current in the external circuit. It has several technological applications in industries and research[1]

Cadmium tellurite bulk cxompound belongs to II-VI class of semiconductor compounds. With a direct band gap of 1.5eV, this compound semiconductor can have different photoresponse properties ranging from far infrared to ultra violet regions. In general, II-VI semiconductor compounds possess high resistivity of the order of 10^3-10^{-6} Ω m which is one of the pre-requesites for enhancing photosensitivity[2]. Based on technological importance of CdTe polycrystalline and nanocrystalline thin films as a potential rich material for photoconversion devices, considerable attention has been given in recent years by research workers for characterization of CdTe nanoparticles and thin films. CdTe possesses a wide range of applications ranging from photovoltaic conversion , high energy flux detectors viz. X-ray and ν-ray detectors[3] to electronic and opto-electronic devices. With this bang gap of 1.5eV, CdTe is well matched to the solar spectrum. Already CdTe based thin film solar cells have been fabricated with efficiencies upto 15.8%[4]. CdTe has been recognized as a leading thin film photovoltaic material due to its suitable band gap and high absorption coefficient. CdTe absorbs over 90% of available photons (hν > 1.5eV) in a 1μm film thickness so that films of 1-3μm are sufficient for thin film solar cells[5]. In view of the economic considerations and such other advantages of CdTe thin films, the detail structural, optical and photo-electrical characterization of chemically synthesized Ce^{3+} doped CdTe nanocrystalline thin films is the prime objective.

II.   Materials and Method

Synthesis of CdTe nanoparticles by SILAR technique requires Cadmium chloride CdCl$_2$ (AR Grade) [Aldrich Sigma] as Cd^{2+} - cation source, Sodium tellurite (AR Grade) Na$_2$TeO$_3$, [Aldrich Sigma, 99.99%] as Te^{2-} – anion source, trisodium citrate as reducing agent, Ammonium hydroxide (NH$_4$OH) as catalyst to adjust the p^H value of the solution. Properly cleaned ITO glass (40 x 25 x 2 mm^3) were immersed into 0.4M CdCl$_2$

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dissolved in 50ml Double Distilled water (DDW) containing ½ .2wt. % PVA and different doping concentrations of Ce $^{3+}$ (2, 5, 8, 10 at. %) . In a typical synthesis of 2 at. % Ce^{3+} doped CdTe nanocrystals, 0.4M of CdCl$_2$ was prepared in 500ml DD water as reserved solution. Secondly, 2 wt. % PVA solution was prepared separately in two beakers as reserved solution. Then 50ml of CdCl$_2$ was mixed with 50ml of PVA and **2 at. % Ce $^{3+}$** prepared by dissolving appropriate amount of Ce(NO$_3$)$_3$ in 5ml of DD water. The entire mixture was stirred electro-magnetically for 5 mins. Properly cleaned ITO glass (3 nos.) substrates were immersed in the solution for 10mins when Cd^{2+} - ions were adsorbed on the substrates. The substrates were removed   and stabilized for 10 mins and then rinsed in running DD water for removal of loose Cd^{2+} - ions.

Now, the substrates were immersed into 0.4M (equimolar) solution of Sodium tellurite Na$_2$TeO$_3$ mixed with 10ml of trisodium citrate   and a few drops of Ammonium hydroxide (NH$_4$ OH) solution at P^H = 8 for 10 mins when Te^{2-} - ions were adsorbed on the Cd^{2+} - ions deposited substrates. The two opposite ions Cd^{2+} and Te^{2-} react to form CdTe (0.4M) equimolar thin films at Ce^{3+} doped 2 at. %. The substrates were then finally rinsed in running DD water and dried in oven. Then the films were annealed at 10^{0}C above room temperature for 24hrs. Similarly, CdTe : Ce^{3+} at doses 5, 8, 10 at. % were synthesized. The detailed morphologica and nanocrystalline structural and optical properties were published in our earlier paper.[6]

To ensure good ohmic contacts between the film and electrodes for photoconductivity measurements, a photo grade purity Ag electrodes of 5.0 x 10.0mm^2 sizes were uniformly vacuum deposited over doped CdTe thin films via properly designed mica-masks inside **HINDHIVAC 12 A** 4 vacuum Coating Unit under vacuum pressure 1.33 x 10 $^{-4}$Pa to achieve Ag/CdTe/Ag gap type cell configuration with 5mm inter-electrode spacing. The cell configurations were successively mounted on a suitably designed mica sample mount and then suspended inside a continuously evacuated air sealed glass jacket using thin enamelled copper wires under vacuum pressure ~ 2.67 Pa achieved by means of a double stage rotary pump. An optical focussing arrangement was made in dark background for illuminating the sample uniformly with a   white light intensity. A tungsten halogen lamp (250W-24V) attached with a parabolic focussing mirror was used for the light source. 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. The dark currents and the currents under illumination were measured with the help of high input impedence (~10^{14}Ω) **ECIL Electrometer Amplifier** under different d.c. bias voltages obtained from a number of series connected dry cells of emf 9 volts each.

III.   Results And Discusion:

3.(i) Film-electrode contact:

The film-electrode contact was examined at Ce^{+3} –ion dozes on the synthesized CdTe films and was confirmed from the I-V characteristics in both current under illumination(I$_L$) and current under dark (I$_D$) as shown in Fig.1. It was observed that the junction was ohmic at low applied voltage in both polarities of applied bias in the films with Ce^{+3} low concentration and fairly ohmic in low and high field regions with increase of doping ranges in the films Fig.2.
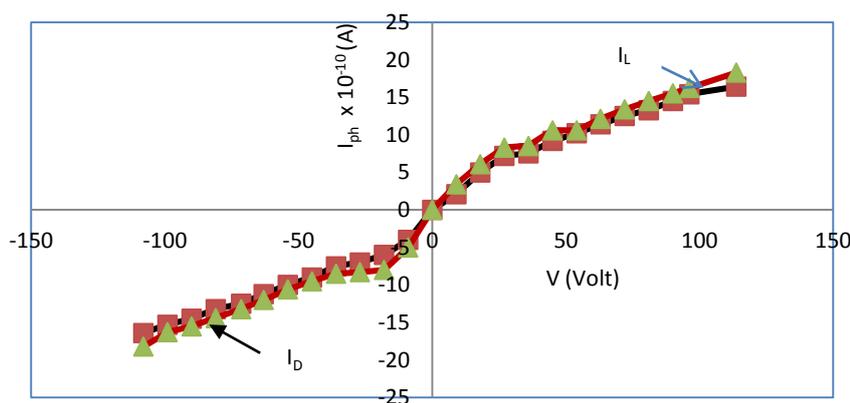
Fig. 1. I-V characteristics of CdTe : Ce^{3+} : 2 at.% at 11000 Lx
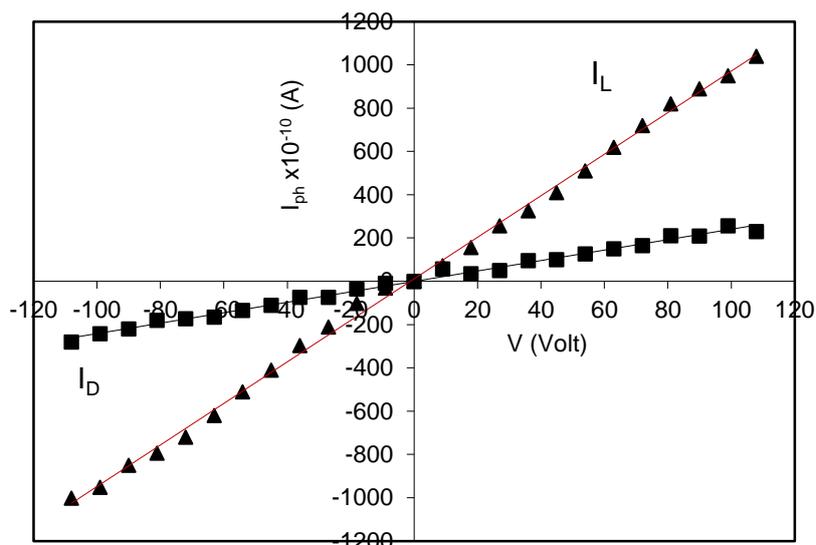
Fig. 2. I-V characteristics under 11000 Lx CdTe :Ce^{+3} 8 at.% film**s**

3.(ii*) Effect on photocurrent and photosensitivity:*

The photoconductivity in a material is the electrical conductivity by carriers in the semiconductor under a suitable photon excitation of definite intensity when a current flows in the external circuit. The change in photocurrent (I_{ph}) with the change in the intensity (φ) of illumination of light in the materials is expressed by the power law relation [7]

$$I_{ph} \, \alpha \, \phi^{\gamma} , \qquad\qquad\qquad\qquad (1)$$

where $I_{ph} = I_L - I_D$, the I_D the current under dark (dark current) and exponent γ represents a number which expresses the basic nature of the carriers transport in the photoconducting material and the value of γ can be calculated from the slope of *InI_{ph} vs. In Φ* plots in the given ambient condition of the host material. The intensity of light *Φ* is defined as the number of photons incident per second on unit surface area of the material under investigation. The variation of *InI_{ph} vs. InΦ* in the nCdTe doped thin films at different doping densities = 2, 5, 8 and 10 at. % under applied bias 36V, 63V and 90V with constant 11,000 Lx white light illumination have been shown in the adjoining Fig.3 (a,b,c &d) respectively. The values of exponent γ calculated from such plots are given in Table - 1. The results show that the values of γ in the host samples are not different from a mean value 0.65.Hence the exponential relation (1) can be expressed in linear form $InI_{ph} = 0.65\ In\Phi$. As
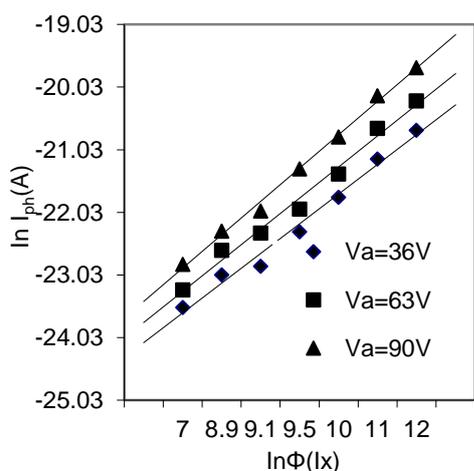
Fig.3(a). InI_{ph} vs. $In\Phi$ of 2 at.% Ce^{3+} : CdTe films illuminated white light.
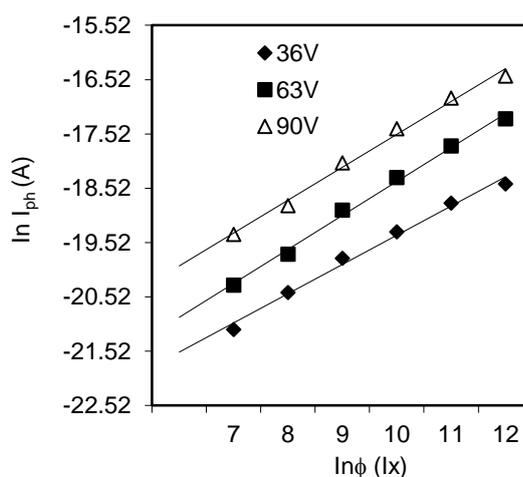
Fig3(b). In I_{ph} vs. In Φ of 5 at. % Ce^{3+} : CdTe films, white light illumination.
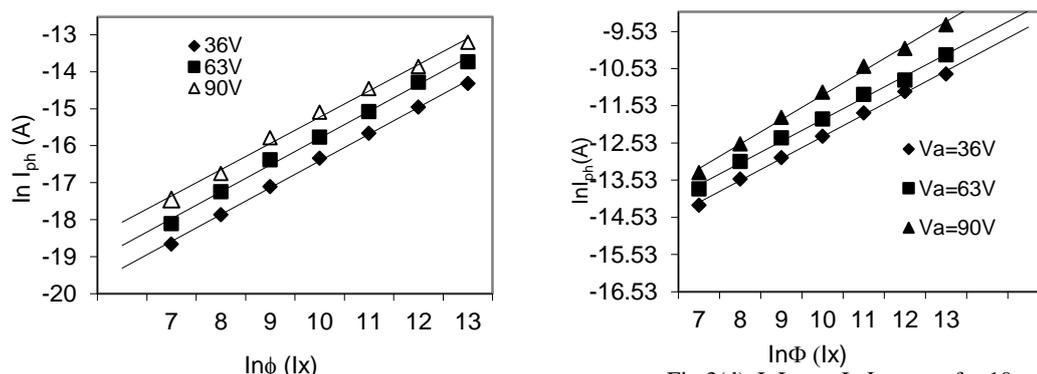
Fig 3(c) . $\ln I_{ph}$ vs ln φ of 8 at.% Ce^{3+} : CdTe films.

Fig.3(d). $\ln I_{ph}$ vs. lnΦ curves for 10 at.%Ce^{3+} : CdTe films.

the exponent γ determines whether the recombination is monomolecular(current conduction by electrons in conduction band or holes in valence band only) or bimolecular (conduction of current through electron –holes recombination), the distinction can be observed from the general relation [8]

Table- 1. Exponent γ in Ce $^{3+}$ ions doped CdTe films, illuminated with 11,000 Lx of WL under different applied bias.

Ce^{3+}-ions doped in nCdTe	Calculated γ- values in doped CdTe films		
	36V	63V	90V
(a) 2 at. %	0.61	0.65	0.60
(b) 5 at. %	0.56	0.64	0.66
(c) 8 at. %	0.76	0.70	0.62
(d) 10 at. %	0.62	0.61	0.72

$$g = C\,[\Delta n^2 + 2n_0\,\Delta n\,] \tag{2}$$

where g is the carrier generation rate, n_0 is the density of thermally generated carriers, Δn is the excess carrier density and C is the capture coefficient at the traps. For bimolecular recombination process where $\Delta n \gg n_0$, and the relation (2) becomes

$$\Delta n = \sqrt{\frac{g}{C}} \quad \text{i.e.} \quad \Delta n \; \alpha \; \Phi^\gamma \tag{3}$$

as g is proportional to the intensity of illumination (φ) and γ = ½ or 0.50. Experimentally for all the films of different doping concentrations under different ambient conditions with white light illuminations, the average value of γ remains practically constant at an average value nearly 0.65. This implies that the transit times of the photogenerated carriers do not have any significant variations within the range of the applied bias and temperatures. Therefore, the bimolecular recombination (*recombination of holes and electrons from valence band to conduction band)* process predominates the photoconduction mechanism in these films [9,10]. Such types of independence of the exponent γ on applied bias and ambient temperatures is also in conformity with the observations of others [11,12].

The curves of the figures 3(a,b,c &d) show that the photocurrent ($I_{ph}= I_L\text{-}I_D$) increases with increase the doping concentrations in the composition of the nCdTe thin films, at fixed ambient temperature and applied bias. This is due to increase of the density of photogenerated carriers and reduction of the grain boundary potential barrier in the depletion regions in the films. The photocurrent also increases with increase of applied bias in the grown CdTe films.

Photosensitivity
The photosensitivity of the as deposited nanocrystalline semiconducting CdTe thin films can also be investigated for technological applications. Photosensitivity is defined as the ratio of photocurrent (I_{ph}) to the dark current (I_D) in the conducting thin films. Hence, we express photosensitivity[13,14],

$$P_s = \frac{I_L - I_D}{I_D} = \frac{I_{ph}}{I_D} \tag{4}$$

Figs. 4(a,b & c) show the change in photosensitivity vs. white light intensity in some chemically grown at *(2at.%, 5at. % and 10at. %) Ce^{3+} : CdTe* films respectively under different applied biases. It is observed that photosensitivity in these thin films increase with increase in the intensity of white photons and applied bias as also shown in the representative Fig.4(d) in a particular CdTe:10 at.% Ce^{+3} film.
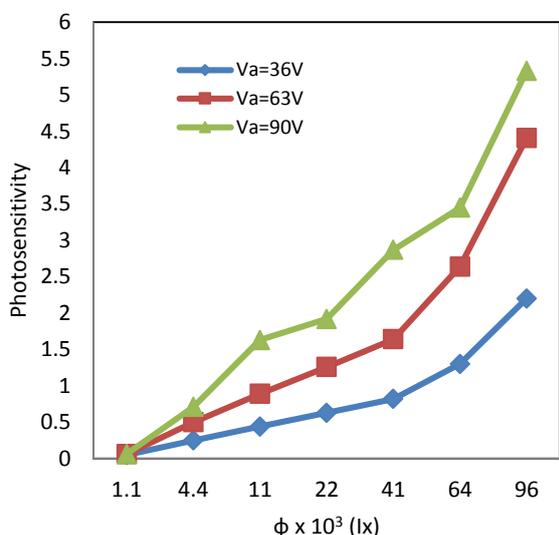
Fig.4(a). Photosensitivity vs. w.l. intensity in 2 at.% Ce^{3+} CdTe films.
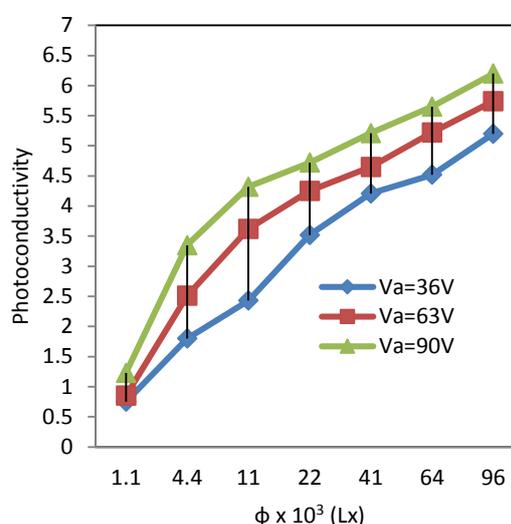
Fig. 4(b). Photoconductivity vs. of w.l. Intensity in 5 at. % of Ce^{3+} CdTe.
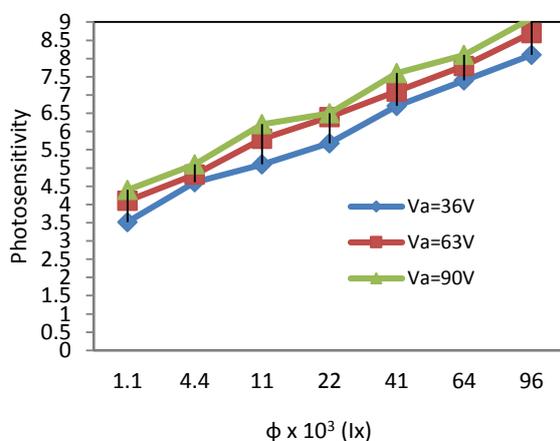
Fig. 4(c). Photosensitivity vs. intensity of w.l. 10 at.% CdTe of Ce^{3+} .
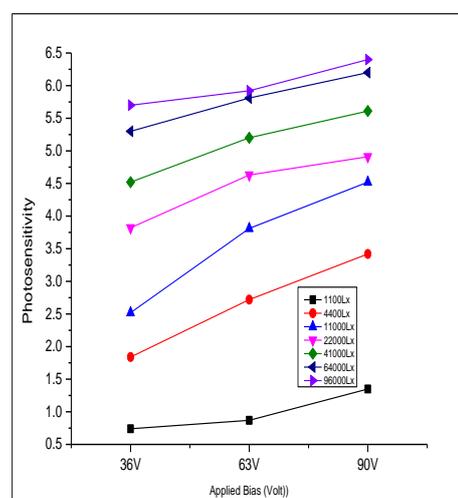
Fig. 4 (d) Photosensitivity vs. Appl. bias in CdTe : Ce^{+3} 10at.% films at diff. int. of w.l.

It is observed that photosensitivity in the CdTe films enhance with increasing of the applied bias as well as intensity of illuminations. The analysis of the curves reveals that photosensitivity in these films is almost independent of applied bias upto 36V at low intensity up to 1100 Lx, but becomes strongly dependence above some threshold intensity. Further, the rate of increase of photosensitivity with amount of Ce^{3+} ions concentrations in the films via the intensity implies that the absorption coefficient of white light becomes higher and some physical parameters like electron - hole traps and donor or acceptor levels are uniformly distributed in the energy gap of the films. The nature of such dependence of photosensitivity in the films' basic parameters ` reveals the presence of large number of defect density. Hence, chemically synthesized by SILAR technique Ce^{3+} : CdTe thin films are found to be highly photosensitivity for technological applications.

IV.   Conclusion

Successive Ionic Layer Adsorption and Reaction (**SILAR**) technique is one of the best techniques for synthesis of nanocrystalline thin films based on economic and time consumptions. Both qualitative and quantitative measurements of low photocurrents ~10^{-9}-10^{-10} A for study of photoresponse properties in thin film semiconductors like CdTe doped and undoped is found possible only in perfect vacuum environment avoiding any ground loop currents. Under such suitable conditions, photocurrents and photosensitivity in the samples enhance with increase of intensity of white light illumination, applied bias and concentration of Ce^{+3} ions in the films. The photoresponse properties in the films is found to correlate with the bimolecular recombination transport mechanisms between carriers through uniform distribution of electron-hole traping centres.

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