

Synthesis and characterization of nanostructures, optical properties of CdTe: Ce³⁺ thin films at doping doses

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Abstract: CdTe thin films deposited with Ce³⁺ at different doping concentration were synthesized by Ionic Layer Adsorption and Reaction (SILAR) technique. The surface structures of the films were studied with FESEM technique and the XRD line profiles of the films revealed with fair growth of nanostructures with decreasing peak intensity with increase of Ce³⁺ doses between 2 at. % - 8 at.% with identical (110) and (111) crystal reflecting planes. The peak intensity is observed enhanced to a maximum value with new (200) plane at Ce³⁺ : 10 at.%. The particle radius in the films were estimated from the broadening X-ray line profiles of maximum peaks of the spectra which approached the quantum dots (QDs) regime. The lattice parameters of the nanocrystals were estimated and observed to be closed agreement with the standard JCPDS data. The size dependent CdTe nanoparticles showed maximum photon absorption blue shift near 375nm wavelength in the UV region ascribed as first excitonic transition as result of reduction of particle radius with increase of band gaps.

Key words: CdTe thin films, doping, quantum dots, FESEM, XRD, optical properties

Date of Submission: 26-01-2019

Date of acceptance: 09-02-2019

I. Introduction

In the past two decades, synthesis of “small particles” by different methods become fascinating field of research in various fields of physics and chemistry. The “small particles” materials now we call nano-materials (1-100nm in diameter) are very interesting materials for scientific reason and technological applications¹ due to their unique characteristics that cannot be obtained from conventional macroscopic materials². More precisely, semiconductors in nanoscale have attracted much attention because of their novel properties originating from quantum confinement effect – the effect produced by trapping the excitons (electrons & holes) in quantum wells incompatible in macroscopic materials and quantum size effects^{3,4,5}. These trapped excitons can be confined into preferred direction- in the form of wires that we call quantum wires, or nanosheets, nanotubes etc. Most studied nanocrystalline semiconductors belong to II-VI and IV-VI groups as they are relatively easy to synthesize and are generally prepared as particles or in thin film form. Cadmium tellurite belongs to II-VI compound semiconductors with direct band gap (1.5eV) and has varied technological applications ranging from photovoltaic conversion, X-ray and v-ray detectors to electronic and optoelectronic devices because of its suitable to solar spectrum. CdTe is also widely used as a buffer layer in infrared detectors using HgCdTe as the sensor element. Recent researchers reported that CdTe is considered for optical waveguide applications and has shown efficient photoluminescence properties at different frequencies depending on sized of the nanoparticles⁶. Several methods may be employed to fabricate CdTe thin layers such as thermal evaporation technique, closed space sublimation, electrodeposition, metal organic chemical vapour deposition, chemical bath deposition (CBD)⁷, Successive Ionic Layer Adsorption and Reaction (SILAR). Among these, SILAR technique is chosen the best for deposition of CdTe thin films from economical and less time consumption to fabricate nanoparticles. The purpose of the present work is to study the effects of doping doses of Ce³⁺ on the nanostructures, surface topology and optical properties of chemically deposited CdTe thin films.

II. Experimental Detail

Synthesis of CdTe nanoparticles by SILAR technique requires Cadmium chloride CdCl₂ (AR Grade) [Aldrich Sigma] as Cd²⁺ - cation source, Sodium tellurite (AR Grade) Na₂TeO₃, [Aldrich Sigma, 99.99%] as Te²⁻ - anion source, trisodium citrate as reducing agent, Ammonium hydroxide (NH₄OH) as catalyst to adjust the P^H value of the solution. Properly cleaned ITO glass (40 x 25 x 2 mm³) were immersed into 0.4M CdCl₂ dissolved in 50ml Double Distilled water (DDW) containing ½ .2wt. % PVA and different doping concentrations of Ce³⁺ (2, 5, 8, 10 at. %). In a typical synthesis of 2 at. % Ce³⁺ doped CdTe nanocrystals, 0.4M

of CdCl₂ 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 CdCl₂ was mixed with 50ml of PVA and 2 at. % Ce³⁺ prepared by dissolving appropriate amount of Ce(NO₃)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 Cd²⁺ - 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 Cd²⁺ - ions.

Now, the substrates were immersed into 0.4M (equimolar) solution of Sodium tellurite Na₂TeO₃ mixed with 10ml of trisodium citrate and a few drops of Ammonium hydroxide (NH₄ OH) solution at P^H = 8 for 10 mins when Te²⁻ - ions were adsorbed on the Cd²⁺ - ions deposited substrates. The two opposite ions Cd²⁺ and Te²⁻ react to form CdTe (0.4M) equimolar thin films at Ce³⁺ doped 2 at. %. The substrates were then finally rinsed in running DD water and dried in oven. Then the films were annealed at 10⁰C above room temperature for 24hrs. Similarly, CdTe : Ce³⁺ at doses 5, 8, 10 at. % were synthesized.

III. Results and discussion

3.1. Structural analysis

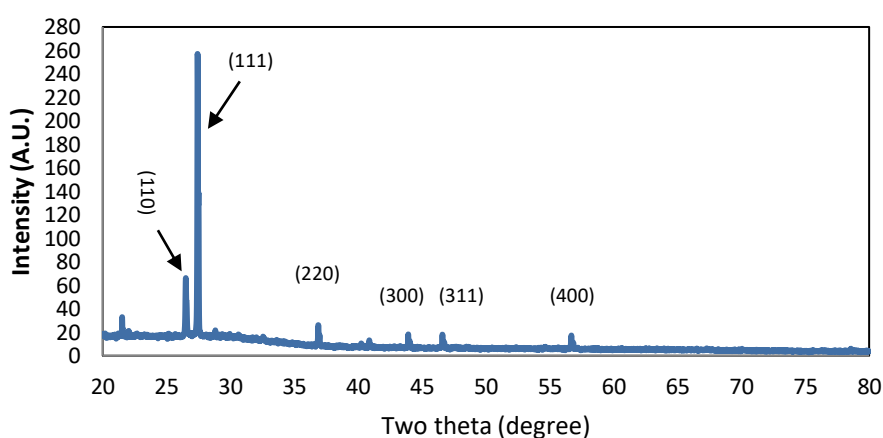


Fig. 1. XRD pattern of CdTe QDs. at Ce³⁺ : 2 at. %

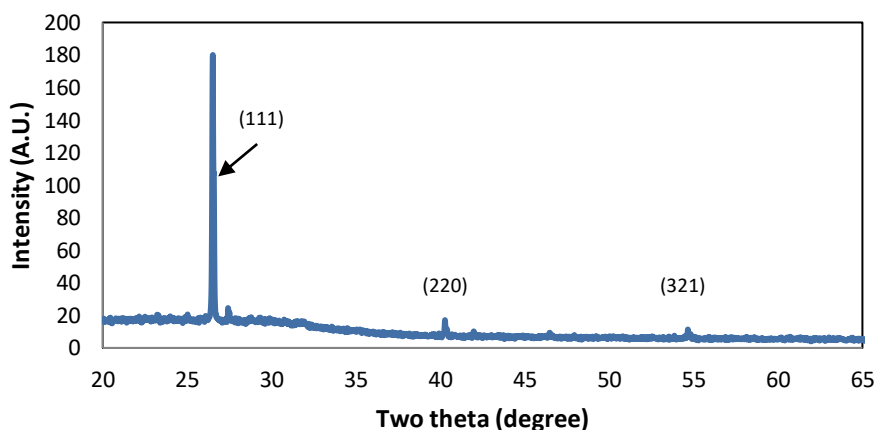


Fig. 2. XRD pattern of CdTe QDs. at Ce³⁺ : 5 at. %.

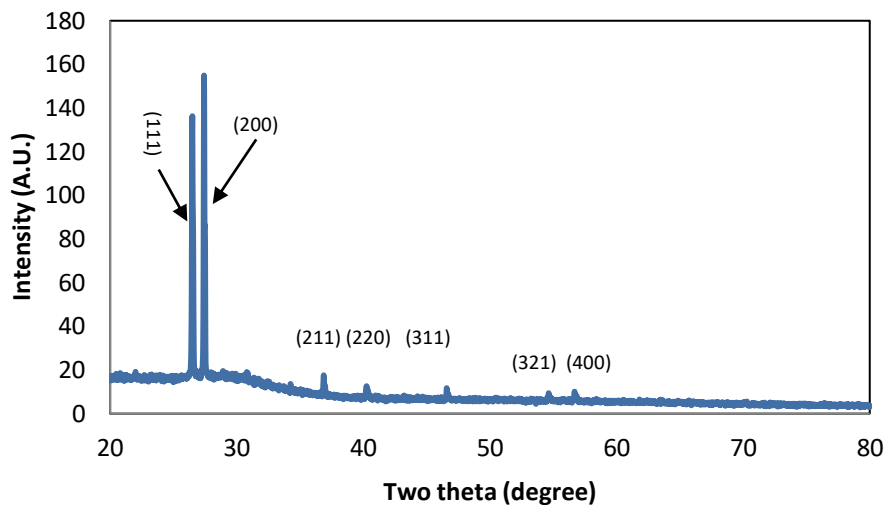


Fig.3. XRD pattern of CdTe QDs. at Ce³⁺ : 8 at. %

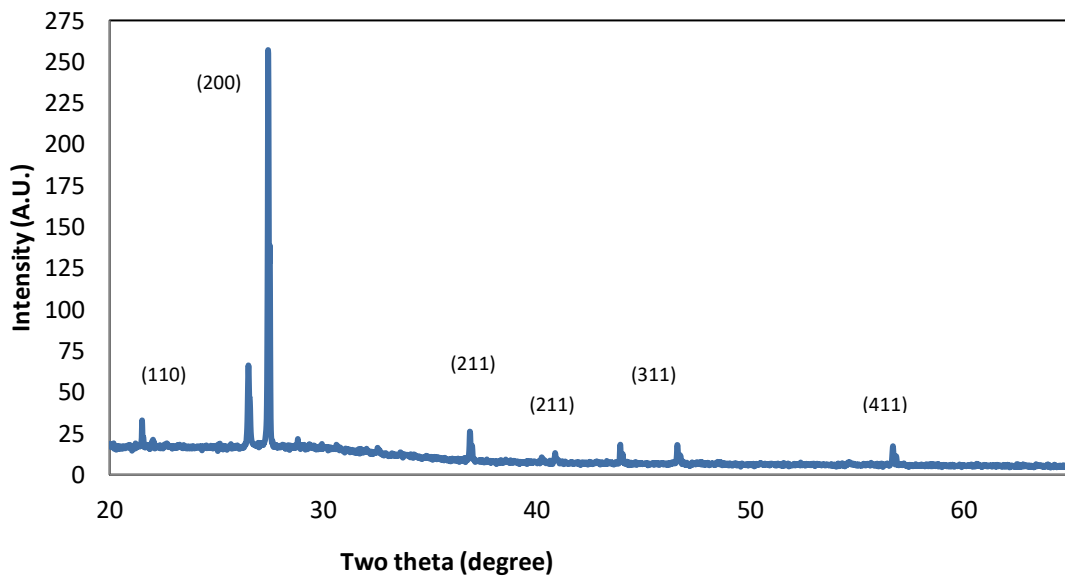
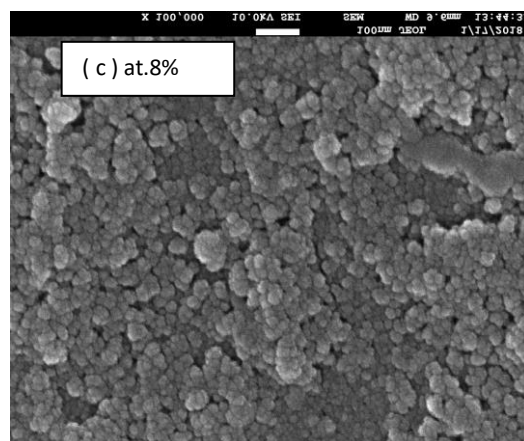
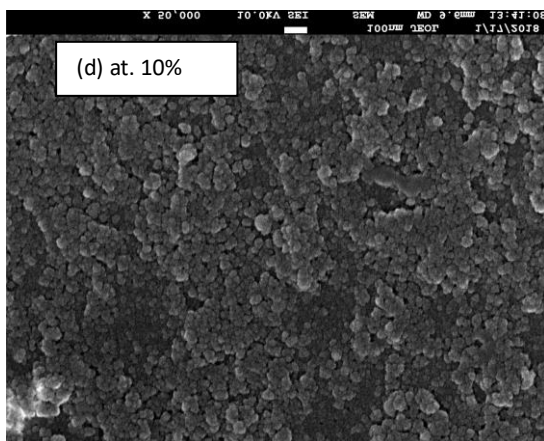


Fig. 4. XRD pattern of CdTe QDs. at Ce³⁺ : 10 at. %.



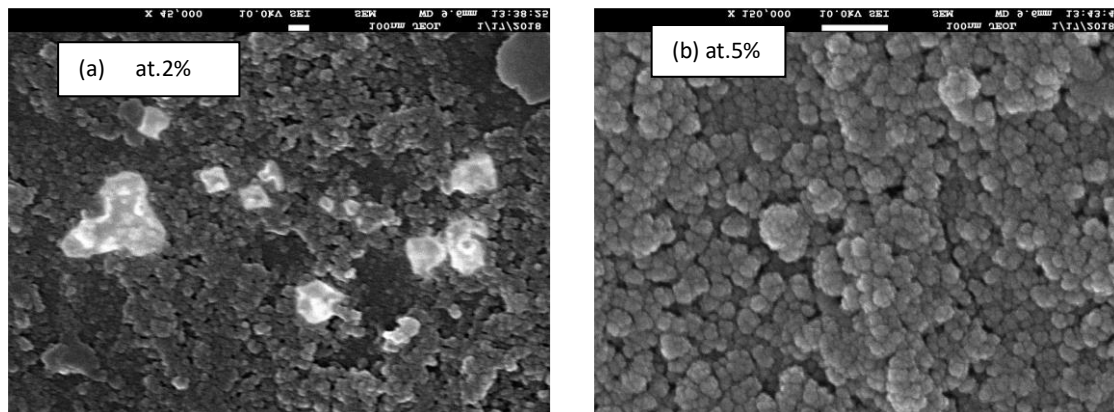


Fig. 5. FESEM images of CdTe :Ce³⁺ nanocrystals at doping concentrations.

X-ray diffraction patterns at low angles of the synthesized CdTe films at different doping dozes were obtained by X-ray diffractometer (Phillips X’pert Pro-Automated Powder X-ray (model APD 1700) diffractometer with CuK_α – radiations (λ = 1.572Å)) as shown in Figures 1-4 and FESEM micrographs of the films in Figure 5. The diffraction patterns show the nanocrystalline growth of the films with cubic zinc blend structure in different reflecting planes. The . Maximum peak intensity was found in 2 at. % doped CdTe film . The lattice parameters of the phase structures of the grown CdTe films at different Ce³⁺ doping dozes were calculated using the relation

$$d_{hkl} = a/\sqrt{(h^2 + k^2 + l^2)} \quad (1)$$

For first order reflection,

$$2d\sin\theta = \lambda$$

for which

$$\sin^2\theta = \lambda^2/4d^2 = \lambda^2(h^2 + k^2 + l^2)/4a^2 = \lambda^2 N/4a^2 \quad (2)$$

where $N = h^2 + k^2 + l^2$, $\lambda = 1.54\text{Å}$ and $a = 6.48\text{Å}$ for bulk(JCPDS-File 15-770).

The (hkl) values and lattice parameters of CdTe crystalline films evaluated at different doping ranges and diffraction angles have been shown in Table-1.

Table-1. CdTe cubic parameters at different doping dozes

Ce ³⁺ : x at. %	//I ₀	2θ value (degree)	hkl	JCPDS a-value (Å)	a _{cal} -value (Å)	JCPDS d-value (Å)	d _{cal} -value (Å)
2	20.5	21.5	110	6.480	5.838	6.869	4.129
	60	26.5	200		6.899		3.450
	260	27.5	200		6.479		3.240
	20	37	220		6.863		2.427
	20	44	300		6.160		2.053
	20	47	311		6.401		1.930
	20	57	400		6.457		1.614
5	180	26.5	111		5.819		3.360
	18	40.5	220		6.294		2.226
	10	46.5	311		6.470		1.951
	10	54.9	321		6.250		1.670
8	138	26.5	111		5.819		3.360
	159	27.5	200		6.479		3.240
	19	37	211		5.945		2.427
	17	40.5	220	6.294	2.226		
	17	47	311	6.470	1.951		
	14	55	321	6.250	1.670		
	14	57	400	6.457	1.614		
10	25	22	110	5.706	4.035		
	75	25.5	200	6.479	5.945	5.386	
	250	27.5	200				
	25	37	211				
	24	41	211				
	18	47	311				
	18	57	411				
18	57	411	5.108				1.540
				6.534	1.540		

The diffraction of X-rays were found most prominent in (200) plane at x = 2 at. %, (111) plane at x = 5 at. %, (200) plane at x = 8 at. % and (211) plane again at x = 10 at. % in CdTe films as a result of enhanced crystalline growth. The particle sizes in the CdTe films grown at x = , 2 , 5 8 and 10 at. % were calculated at maximum intensity at FWHM using Scherrer's relation ⁸

$$D_{hkl} = k\lambda/\beta_{\theta/2}\text{Cos}\theta \quad (1)$$

where the value of shape factor is 0.94, $\beta_{2\theta}$, the width of the peak at half of the maximum peak intensity and θ the Bragg angle. The estimated values of the particles sizes are shown in Table-1.

Table-2. Particle dimension in synthesized CdTe films

Sl. No.	Doping doze	2 θ_2 -value (degree)	2 θ_1 -value (degree)	D _{hkl} -value (nm)
(a)	2 at. %	27.9	27.2	24.2
(b)	5 at. %	26.8	26.3	36.3
(c)	8 at. %	27.9	27.0	14.5
(d)	10 at.%	27.8	27.1	24.2

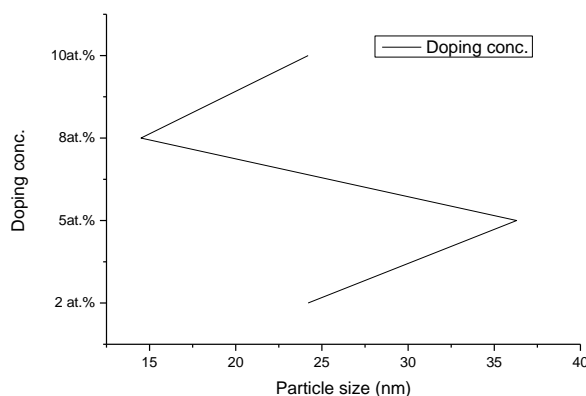


Fig.6. Particle size vs. doping conc. relation in CdTe film.

The results show that the size of the particles in the synthesized CdTe films at different doping concentrations are in nano-crystalline regime closed to QDs. The lattice parameters of the phase structure of the grown CdTe films at different doping dozes were calculated using the relation

$$d_{hkl} = a/\sqrt{(h^2 + k^2 + l^2)} \quad (2)$$

For first order reflection,

$$2d\text{Sin}\theta = \lambda$$

for which

$$\begin{aligned} \text{Sin}^2\theta &= \lambda^2/4d^2 = \lambda^2(h^2 + k^2 + l^2)/4a^2 \\ &= \lambda^2 N/4a^2 \end{aligned} \quad (3)$$

where $N = h^2 + k^2 + l^2$, $\lambda = 1.54\text{\AA}$ and $a = 6.48\text{\AA}$ for bulk(JCPDS-File 15-770).

The (hkl) values and lattice parameters of CdTe nanocrystalline films at the doping ranges and diffraction angles have been shown in Table-1. Seven major peaks at about diffraction angles 22,25.5, 27.5,37, 41, 47 and 57 degrees were observed with reflection planes (110), (200), (211), (211), (311) and (411) respectively with cubic phase structures at the growth CdTe films at autimum Ce³⁺ : 10 at.%. The diffraction of X-rays were found most prominent in (200) plane at diffraction angle 27.5 degree. The peak intensity was observed to decrease with increase of the doping concentration in the synthesized CdTe nano-crystalline films.

3.2. Optical properties in the films.

The figure7shows the absorption vs. wavelength curves of the CdTe nanocrystals synthesized at different molars obtained from UV-vis. Spectrometer (model : Lamda 35LS 35, Parkin Elimer 2008 installed at NIT, Manipur). CdTe is a direct band gap semiconductor. The absorption coefficient, α in the films can be correlated to the photon energy as^{9,10}

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

where E_g is the energy band gap between the valence and the conduction bands, A is a constant being different for different transitions, and n is a constant being equal to 1 for direct band gap semiconductor.

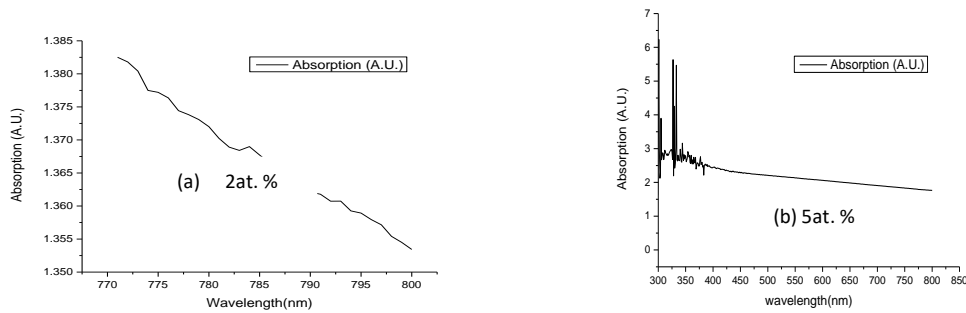


Fig.7(a). Abso. vs. wavelength of CdTe :Ce³⁺ Fig.7(b). Abso. vs. wavelength of CdTe :Ce³⁺

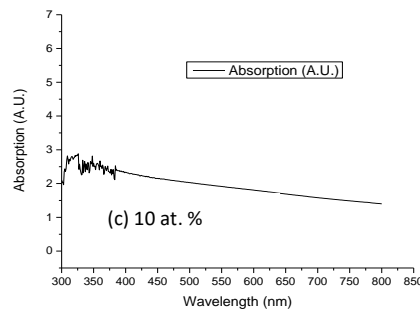


Fig. 7. Absorption vs. wavelength in CdTe films at Ce³⁺ doping concs.

The absorption coefficient, α is found to enhance with increasing doping concentrations within 350 – 800 nm wavelength range. The enhancement of the absorption in lower wavelength ranges may be attributed due to increase of agglomeration of CdTe nanoparticles under quantum size effect which absorb more photons of lower wavelengths with less transmissions. The study of the optical absorption spectra shows absorption peak at 375 nm wavelength which exits in the lower blue spectral side. The blue shift of the absorption edge indicates decreasing the grain sizes in the films¹¹. The study of the optical band gaps with different molar concentration in the films shows an increase in band gap with increasing .

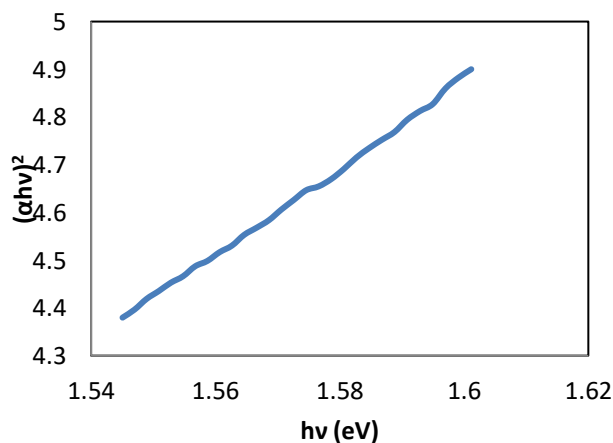


Fig. 8 (a) $(\alpha hv)^2$ vs. hv plot of CdTe at 2 at. % of Ce³⁺ doped film.

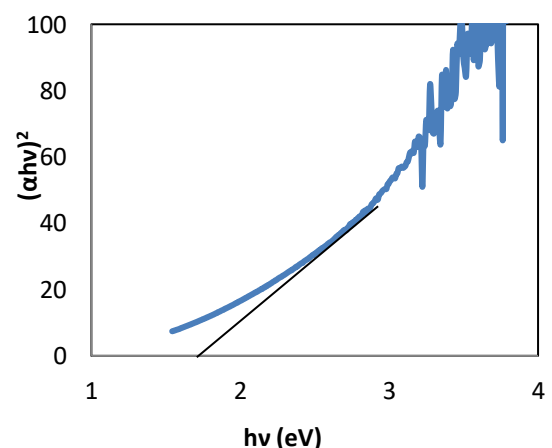


Fig.8(b). $(\alpha hv)^2$ vs. hv curve of CdTe at 5at.% of Ce³⁺ doped film.

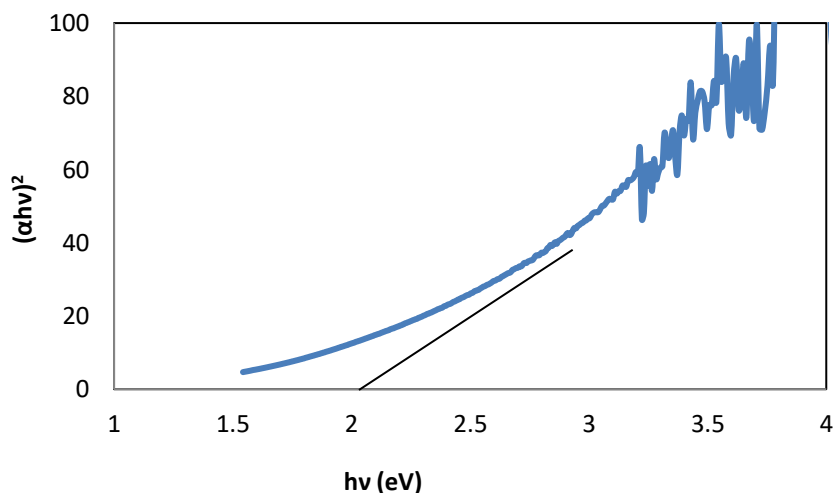


Fig.8 (c) $(\alpha hv)^2$ vs. $h\nu$ curve of CdTe at 10 at. % doped Ce³⁺ film.

doping concentrations. The variation of incident photon energy vs. photon absorption energy in the synthetic doped CdTe nano-crystalline films is shown in Fig. 8 (a, b & c). The intercepts of the extrapolated curves show that the energy band gaps in the doped CdTe films increase with increase of doping concentrations of Ce³⁺ ions in the crystals. The linearity of extrapolated portion in the curve explains the direct optical band gap nature of the synthesized CdTe semiconducting thin films.

Table-3. Energy band gaps in doped CdTe films

Sl. No.	Ce ³⁺ -doses in the films	E _g (eV)
(a)	2 at. %	1.54
(b)	5 at. %	1.75
(c)	8 at. %	1.82
(d)	10 at. %	1.90

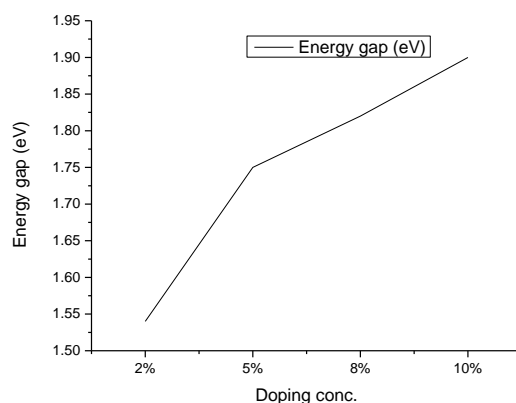


Fig.9. Energy gaps vs. doping conc. in CdTe films.

The experimental values of the energy gaps in the doped CdTe films is shown in Table-3 and the variations of band gaps with doping doses is shown in Fig.9. The mechanisms of chemically deposited CdTe thin films at the varied doping ranges will find significant contributions in technological applications like fabrications of thin film solar cells, photo-detectors and many other photo-electronic devices.

IV. Conclusion

Successive Ionic Layer Adsorption and Reaction (SILAR) technique is found to be less time consumption method for synthesis of inorganic semiconducting thin films. The surface structure and crystal structures of the CdTe doped with Ce³⁺ ions at different doses at room temperature were observed to be uniform and found to be cubic zinc blend structure with multifaceted diffraction planes with most preferential

reflection along (200) plane. The size of the particles in the films were found approaching quantum dots sizes (1-10nm). The experimental values of lattice parameters of nano-cubic phases were determined and found below the standard values as a result of quantum confinement effect. The optical analysis of the films showed that the absorption co-efficient is found to enhance with increase of Ce³⁺ ions doping concentrations and is expected due to agglomeration of quantum size nanoparticles which absorbs more photons of lower wavelength with less transmission. The photon absorption edge in the films was found at 375nm wavelength in the lower blue spectral side. This blue shift of absorption edge indicates decreasing the size of grains in the films. The study of change of incident photon energy vs. absorption coefficient of photon in the films shows increase of optical band gaps with increase of Ce³⁺-ion concentrations.

Acknowledgement

The authors thank to Centre for Nanotechnology, IIT Guwahati, Assam for providing FESEM facility and NIT, Manipur for XRD and UV-vis spectrophotometer for structural and optical analysis of the films.

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S. Jogita Devi. "Synthesis and characterization of nanostructures, optical properties of CdTe: Ce³⁺ thin films at doping doses. " *IOSR Journal of Applied Physics (IOSR-JAP)* , vol. 11, no. 1, 2019, pp. 19-26