Structural, morphological, electrical and optical properties of Zn doped CdTe thin films

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Cadmium Zinc Telluride (CdZnTe) is a ternary II-VI undeviating band gap semiconductor with cubic zinc blende formation and it is a propitious material for ambient temperature x-ray as well as gamma ray sensor detectors. Cadmium Zinc Telluride (CdZnTe) thin layer coating were developed on nickel substrate by chemical bath deposition in non-aqueous approach. The as grown films were inspected by X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM), Scanning electron microscope, Fourier transform infrared spectroscopy (FTIR), PL spectra, UV spectra, Raman spectroscopy and Four-Probe analysis. Studies tell that as grown films are poly-crystalline in nature along with cubic zinc blende formation. The structural properties like crystallite size, lattice constant, micro strain as well as dislocation density were evaluated. FESEM and SEM analysis reveals that the as developed films are smooth and equal sized uniform spherical grains distributed in single state as well as in cluster form. The average size of grain film is observed to be 12.33 nm. Optical study reveals the broad transmittance escorted by the band gap energy of 2.2 eV. Electrical study reveals that resistivity of as grown film is $5.1 \times 10^5 \Omega\text{-cm}$ at room temperature.

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1. Introduction

The ternary CdZnTe is a II-VI direct bandgap semiconductor having outstanding properties is one of the most propitious materials for ambient temperature x-ray and gamma ray detectors for the reason of its short leakage currents along with excessive quantum efficiency in sensors detectors [1]. CdZnTe compound is taken to be an interesting subject in order to convey out exotic electric and optical properties. CdZnTe has a undeviating ternary aperture for all alloys composition and is tuneable from 1.5 to 2.3 eV at ambient temperature [2]. It shows many physical features stand in need of detector operation, for example way up atomic number (Z) for well requested radiation atomic interconnection, big enough bandgap for high volume resistivity have need of maintaining short noise associated with outflow current in the sensor. A substantial cross-section area for the photoelectric sucking up of gamma rays mandatory for efficient transformation of the gamma rays energy into electrical energy, enormous inherent mobility lifespan ($\mu\tau$) product and lessen electronic disturbance. This ternary composite has a cubic zinc blend – type lattice accompanied by atomic number in close proximity such like of CdTe [3]. CdZnTe has been utilized in solid state appliances such as light emitting diodes, photo detectors/sensors and solar cells. In recent years, the technology of CdZnTe has matured and it finds application in nuclear medicine, national security, space sciences. In nuclear medicine implementation associate with imaging approach such as x-ray or gamma-ray tomography, x-ray fluorescence. In national security implementations associate essentially with locating, keeping track, or recognizing radioactive substance for instance nuclear weapons inspection as well as nuclear plant tracking for

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environmental reformative and well-being. In space sciences implementations associate with high energy focusing telescope (HEFT) [4].

Lately copious kinds of film depositing methods have been acquired to form CdZnTe thin film layers including electrodeposition [5] [6], thermal evaporation [7], magnetron sputtering [8], closed spaced sublimation [9] and chemical bath deposition [10]. Among all these methods of working, the chemical bath deposition (CBD) technique is the solitary simplest and the most economical technique. It also provides high deposition rate and large area deposition as compared to other techniques [11] [12]. So, it meets the requirement for the fabrication of photovoltaic devices [10].

In this work we describe the building and identification of CdZnTe thin film grown on nickel substrate by CBD in non-aqueous medium as non-aqueous mode gives additional flexibility and is further advantageous as considered to aqueous mode. In non-aqueous method we can work on elevated temperature providing us wide scale of substrate choice. Unlike aqueous mode there is most certainly no evolution of hydrogen producing the film build-up free from pin holes. The deposited film was identified by field emission scanning electron microspore, x-ray diffraction and optical transmission in the detectable and rear infrared.

2. Experimental Procedure

The osmolarity was put together by employing AR grade 0.05M TeO_2 , 0.05M cadmium acetate ($\text{Cd}(\text{CH}_3\text{CO}_2)_2$), 0.125M NaBH_4 and 0.5M ZnCl_2 deliquesce in 40ml of ethylene glycol. First, the 40ml of ethylene glycol was taken in a beaker and a modest stirring was persisted out by a magnetic stirrer for 2 hours and temperature of the blended solution was persisted at 160°C . When the temperature of the compound was reached to 160°C we add 0.05M TeO_2 and stirred for 10min then we add 0.05M Cadmium acetate and stirred for 5min after that we add 0.125M NaBH_4 to the solution and stirred for 2hours. At last, 0.5M ZnCl_2 was introduced in the solution and stirred for next 2hours. With the assist of rigid prop up, Ni plate having dimensions 2cm X 1cm was dipped into the electrolyte and the film deposition was sustained out for 15 minutes. The deposition was blackish in colour. The film was cleaned with DI water and parched at room temperature. The as deposited film was examined/studied in phase of their structural form & composition as well as optical properties to observe their solid-state characteristics.

3. Results and Discussion

3.1. Structural Analysis

XRD patterns of as grown CdZnTe films settled on Ni substrate are shown in Fig.1. The developed film shows good adhesion and physical stability. The XRD spectra is sustained in the span of $20-80^\circ$. From the figure it is perceived that the CdZnTe thin film stipulate that the indicated peaks located at $2\theta = 23.01, 40.45, 51.27, 56.9, 67.7$ and 81.4 arises on the stretches and the peaks are recognized as (111), (220), (222), (400), (331), (420) and (511) diffraction planes of the cubic zinc whisk structure [13]. The cubic phase with zinc blende structure of the CdZnTe thin coating is found to be viable polycrystalline with a (111) favoured orientation [14]. It is also observed that as deposited CdZnTe thin film shows phase exclusion, i.e., two aspects (ZnTe and CdTe) with a (012) preferred orientation for ZnTe and (222) & (331) preferred orientation for CdTe. Along with that it shows peaks of Cd and Te with preferred orientation of (101) and (110) for Cd and (220) for Te. The average crystallite dimension (D) was computed using Scherrer formula, $D = (K\lambda)/\beta\cos\theta$ [15]. While the lattice constant (a) of cubic state and interplanar spacing (d) work computed by the 2θ values of (111) peak and Bragg's equation for the cubic arrangement in addition all these are listed in Table 1.

Fig. 1. XRD spectra of as deposited CdZnTe thin film.

Table 1. Shows the crystallite size (D), Lattice Constant (a) and inter-planer spacing of as-grown CdZnTe thin films.

S.No	Average Crystallite Size(D) (nm)	Lattice Constant(a) (Å°)	$d_{(hkl)}$ (Å°)
1.	68	6.7	3.8609

Micro strains flourished in the films were estimated using the subsequent equation [16].

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (1)$$

The average crystallite dimension of as deposited CdZnTe come about 68nm. The lattice unchanging factor of CdZnTe as cast thin films was found to be 6.7Å°. It is familiar that the lattice tension can be evolved in the as grown thin layer coating occurring to disparity in deracination of the atoms concerning their reference lattice position [13]. The dislodgment density of the as deposited CdZnTe thin films were figured out adopting Williamson- smallman relation

$$\delta = \frac{1}{D^2} \quad (2)$$

The calculated 2θ and miller planes of as grown CdZnTe thin layer coating films are given in table 2. The micro-strain as well as dislocation density of the as deposited CdZnTe films are listed in table 3.

Table 2. 2θ, d and miller-indices of as-deposited CdZnTe thin film.

		Observed Value			Standard Value	
Compound	2θ	“d”	Miller-indices	2θ	“d”	Miller-indices

CdZnTe as deposited	23.01	3.860	(111)	23.74	3.743	(111)
	40.45	2.227	(220)	40.60	2.218	(220)
	51.27	1.780	(222)	50.50	1.805	(222)
	56.90	1.616	(400)	56.83	1.618	(400)
	67.70	1.382	(420)	66.83	1.398	(420)
	81.40	1.180	(511)	80.91	1.197	(511)

Table 3. Shows dislocation density and micro-strain of the as deposited CdZnTe films.

S.No	Dislocation Density($\times 10^{10} \text{ cm}^{-2}$)	Micro-strain ($\times 10^{-3}$)
1.	2.163	29.39

3.2. Surface Morphology and Elemental Compositional Study

Fig. 2 shows the surface diagnosis of the as grown CdZnTe thin layer coating film using FESEM and SEM. 25KX and 50KX magnification is taken for the FESEM and SEM photography. From the figure it is observed that the as grown film shows smooth and equal sized uniform spherical grains. The spherical grains are distributed in single state as well as in cluster form over the complete top surface of the film. This shows the crystalline quality of the CdZnTe film. The FESEM and SEM of as grown CdZnTe film show that the elemental particles of CdZnTe have agglomerated and has resulted in the origination of nano clusters [17]. It is also evidence from the contrast of the film that the grains of the as grown film are condensely packed, free from perforation voids and pits and the mean grain size is found to be 12.33 nm.

Fig. 2. Morphology of as-grown CdZnTe (a, b) FESEM of CdZnTe at 25KX and 50KX, (c,d) SEM of CdZnTe at 25KX and 50KX.

The elemental composition analysis of as cast CdZnTe thin film is depicted in fig.3. The EDAX pattern were documented in the binding energy of 0-20keV. The peaks in fig.3 unveiled the existence of cadmium (Cd), tellurium (Te) and zinc (Zn) in the as cast CdZnTe thin films. The

atomic % and weight % of the film are comprised in Table 4. The mean atomic % of Cd, Zn and Te is observed to be 17.64%, 1.44% and 80.92% respectively. According to Subhash Chander et.al [18]. The elemental proportion of CdZnTe thin layer coating films have ratio of Zn much lesser than cadmium and tellurium. The EDAX analysis of as developed CdZnTe thin film reveal to the formation of stoichiometric film.

Table 4. Shows atomic% and weight % of as-grown CdZnTe thin film.

S.No.	Element	Atomic%	Weight%
1.	Cd	17.64	9.91
2.	Zn	1.44	1.39
3.	Te	80.29	88.71

Fig. 3. EDS spectra of as- grown CdZnTe thin films.

3.3. FTIR Analysis

Fig. 4 depicts the FTIR spectra of as developed CdZnTe thin films. The CdZnTe specimen shows the presence of hydroxyl group, carboxyl group and C-H group. In addition to that it also shows C-O stretching. The broad peak at 3278.99cm^{-1} indicates the existence of OH stretching which originate due to atmospheric pressure [19]. The small peak at 1330.88cm^{-1} is ascribed as the C-H bending bond structure of the functional category of alkanes [20]. The peaks at 921.97cm^{-1} reveals the presence of bending vibration of alkenes ($=\text{C-H}$) [21]. The peak at 1072.42cm^{-1} is characterized as stretching mode of aliphatic amines [22]. The peak at 682.80cm^{-1} is attributed on account of bending mode of aromatic C-H functional group [23]. The absorption band occurred corresponds to wave number 856.39cm^{-1} feasibly ascribed to the stretched vibrations of CdZnTe thin layer coating film [13]. The different functional groups appeared in as deposited CdZnTe thin film is shown in Table 5.

Fig. 4. Shows FTIR spectra of as-grown CdZnTe thin films.

Table 5. IR frequencies and vibrational assignments of as deposited CdZnTe film.

S.No.	Positions(cm^{-1})	Assignments
1.	3278.99	O-H
2.	1330.88	C-H
3.	921.97	=C-H
4.	1072.42	Aliphatic amines
5.	682.80	C-H
6.	856.39	CdZnTe

3.4. Optical Properties

3.4.1. UV-Visible Analysis

The optical absorption stretches of as deposited CdZnTe film were characterized at ambient temperature in the wavelength span of 200-800nm. We know that the CdZnTe is a direct energy gap semiconductor, and its energy gap is estimated by tauc relation $(\alpha h\nu)^2 = A(h\nu - E_g)^{1/2}$ [24][37]. Here, A is the proportional constant, h is the plank's unchanging factor, ν is frequency, E_g is the bandgap and α is the absorption coefficient. Fig.5 depicts the optical absorption stretches of CdZnTe thin layer film which is a plot of $(\alpha h\nu)^2$ vs energy ($h\nu$) and energy gap (E_g) of as grown CdZnTe is observed by extrapolation of the incurve for $(\alpha h\nu)^2=0$. The energy band width of as grown CdZnTe is found to be 2.2eV in as deposited case. The outcomes are in agreement with reported work [25] [26] [27] [13]. More or less linear essence of tauc plots indicates CdZnTe is a direct energy gap semiconducting material. It is reported that the energy gap for doped and pure CdTe nanocrystals are bigger. The shoot up in band gap is mainly caused by the following two reasons: firstly, due to alloying with higher band gap materials and secondly the quantum restraint of the levels within the nano crystallites [28].

Fig. 5. Shows Band gap of as-grown CdZnTe thin films.

3.4.2. Photoluminescence Spectroscopy Analysis

Fig. 6 shows the photoluminescence stretches of as grown CdZnTe. The photoluminescence spectroscopy, often referred to as PL is a non-destructive spectroscopic method frequently used for the examination of intrinsic and extrinsic possessions of both bulk semiconductors and nanostructures. The intensity and spectral content of this photoluminescence is undeviating measurement of various supreme material properties. In this technique excitation is given by laser light escorted by energy much massive than the optical band gap. As evident from the figure that as grown CdZnTe thin films shows a fluorescence peak at 374nm along with that it shows broaden emission spectra at 448nm and 469nm, respectively. This broaden emission was due to particle size distribution of CdZnTe nanocrystalline thin films [29][30][31]. From the figure it is also observed that the lesser wavelengths are imputed to smaller size CdZnTe quantum dots and towering wavelengths are imputed to bulk CdZnTe crystals. Doping Zn with CdTe thin films results into a broaden in emission peak at 469nm is evidence of deep trap emission and indicates the deposition of CdZnTe nanocrystalline thin film [32].

Fig. 6. Shows PL spectra of as-grown CdZnTe thin film.

3.5. Raman Analysis

Raman spectroscopy is an alternative and convenient method to identify materials phases and determine the degree of crystallinity of thin film. In this technique, vibration, rotation, and other-low-frequency modes in molecules are observed based on inelastic scattering of

monochromatic radiation. The Raman spectrum obtained using the 785nm wavelength with an exposure time of 10 sec and 0.1mW of power at the sample, distinctly shows a Raman peak at 140,166 and 332 cm^{-1} , which according to the refs. [33], referred to a transverse optics (TO) whereas Longitudinal optics (LO) of phonon mode CdTe of as deposited. Raman Spectroscopy have been successfully applied to the detection of the commonly found Te inclusions in crystalline CdTe. The Raman cross-section of the A1 mode of crystalline Tellurium differs than that of LO mode of crystalline CdTe. For these reasons, Te inclusions in CdTe detected by Raman scattering are not necessarily seen by X-Ray technique. The Raman Spectrum of a crystalline material can only show those modes with ω difference from zero at $q \approx 0$, the Raman spectrum of an amorphous material usually resembles its whole vibrational density of states (DOS), with broadened bands and modulated by frequency-dependent terms that reflect the symmetry of the local atomic environment. This is because the conservation of momentum selection rule for Raman scattering is no longer applicable in the amorphous state, causing all the vibrational modes to become Raman active (and IR active) in principle [38]. This kind of analysis has been applied to other semiconductors. Fig. 7 shows the peaks characteristics CdTe; one of them is at 119 cm^{-1} , secondly at 139 cm^{-1} , thirdly at 166 cm^{-1} and fourth is at 332 cm^{-1} (LO) which correspond to the A1 and E modes of Te, the Longitudinal Optical (LO) phonon, and 2LO phonon vibration mode of CdTe, respectively. It is noted that Te/ Raman modes are usually detected in CdTe samples, which may originate from the presence of little Te precipitates [34][35].

Fig. 7. Raman spectra of as-grown CdZnTe films.

3.6. Electrical Properties

3.6.1. Resistivity Measurement

The resistivity of the CdZnTe film was calculated using four probe techniques. The resistivity(ρ) was calculated by equation, $\rho = \frac{V}{I} \times 2\pi S$, where; V is the difference in potential between inner probes in volts, I is the current into and out of the outer pair in ampere and S is the probe distance in cm (0.200cm). The resistivity of CdZnTe was estimate in the temperature extent from 303 to 363 K. The resistivity of CdZnTe at room temperature was found to be $5.1 \times 10^5 \Omega\text{-cm}$. In case of semiconductor as temperature increases resistivity goes down. Fig.7. shows the electrical resistivity of as grown CdZnTe. From the figure it is perceived that as the temperature surges resistivity decreases since the electrons in the valence band get excited and jump into the conduction band and hence the conductance increases resulting in the decreasing of resistance. As resistance is directly proportional to resistivity, resistivity decreases, too [36]. From the plot $\log_{10}\rho$ Vs $1/T$ we get a curve which is linear at higher temperatures. Therefore, width of the energy gap may be induced from the slope of the linear portion of the experimental curve. The energy gap can be calculated from the expression, $E_g = 2.303 \times 2K \Delta \log_{10}\rho / \Delta T^{-1}$, where K is the Boltzmann's constant. The band gap is found to be 1.98eV which is in agreement with band gap calculated from

tauc formula and reported work (band gap varies from approximately 1.4 to 2.2eV) [13][25][26][27].

Fig. 7. Resistivity of as-grown CdZnTe thin films.

4. Conclusion

The cubic zinc whisk CdZnTe thin films were produced conveniently on Ni substrate applying chemical bath deposition approach in non-aqueous mode. The optical and solid-state effects of as grown CdZnTe thin film were studied by different technique. Cubic zinc blende phase of CdZnTe is observed by XRD. The FESEM and SEM photograph show consistent, condensed, and void free surface. The stoichiometry of the as grown film is entirely alike to the desired matter with some surplus Te in the film. Band gap of the as grown film was premeditated from the optical absorption stretches as 2.2eV. The stretching vibration made of as grown film was observed by FTIR at 856.39cm^{-1} . The electrical resistivity of CdZnTe was found to be $5.1 \times 10^5 \Omega\text{-cm}$. Photoluminescence studies show deep trap emission. CdZnTe film shown have good characteristics to be used as photovoltaic, photo electrochemical cell and sensor applications. The Raman analysis shows the phonon vibration mode of CdTe i.e., LO and 2LO mode at 166.2 and 332.7 cm^{-1} , respectively.

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