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ROLE OF SUBSTRATE TEMPERATURE ON NANAOCRYSTALLISATION OF CdTe THIN FILMS

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In the present investigation, nanocrystalline Cadmium Telluride (CdTe) thin films are deposited on glass substrates by thermal evaporation method. The films are deposited at various substrate temperatures of 573 K, 623 K, 673 K and 723 K. Structural characterization is carried out using X-ray diffraction (XRD) technique. XRD studies reveal nanocrystalline nature of the films. Scanning Electron Microscopy (SEM) is employed to investigate the surface morphology. SEM studies indicate that the nanograin formation begins at 573 K. However, increase in substrate temperature leads to grain agglomeration. The optical characterization is carried out using UV-Vis spectrophotometer. It is observed that the bandgap value is dependent on substrate temperature. All the experimental results indicate that the substrate temperature plays a major role in nanocrystallisation of CdTe thin films. This paper aims at studying the role of substrate temperature in CdTe nanopahse formation.

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1. Introduction

Nanocrystalline thin films of Cadmium telluride (CdTe) have drawn considerable interest due to their potential applications in the field of optoelectronic devices such as solar cells, high efficiency thin-film transistors, lasers, LED, electroluminescent devices, IR detector, photovoltaic etc **[**1-3**].**

Currently nanocrystalline thin films of CdTe are deposited using several deposition methods like electro deposition, sputtering, close spaced vapor transport, spray pyrolysis and metal organic chemical vapor deposition [4-8].

In the present work, thermal evaporation method is used for preparation of nanocrysatlline CdTe thin films. Generally thermal evaporation method is used to deposit polycrystalline films. However recently this technique is popularly used for deposition of nanocrystalline thin films [9].

The morphology (size and shape of the crystallites) and the texture (preferential orientation of the crystallites) are the two most important properties for describing the microstructure of the film. It has been observed that the morphology is strongly dependent on the deposition parameters such as the substrate temperature. [10]. Hence optimization of substrate temperature is essential to get the desired microstructure of the thin film.

Thus in the present work an attempt is made to study the role of the substrate temperature in formation of nanocrystalline CdTe thin films.

When the thin films are deposited using thermal evaporation method, the nucleation of grains begins with the impingement of a vapor particle (atom) on the substrate. The particle can

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either be reflected from the substrate or be (physically) adsorbed. Depending upon the impingement energy, a physically adsorbed particle called as ad-atom, can diffuse over the substrate and re-evaporate or it can get attached to the substrate at a site where its energy is at a local minimum [11]. When more vapor particles impinge the substrate, they exhibit the similar behavior. If two or more particles form a grain i.e. if they nucleate, the possibilities for migration or re-evaporation of ad-atoms from the substrate become smaller [12].

It is reported that if the ad-atom mobility is very low, very few nucleation centers are formed which may result in formation of amorphous film. However if the ad-atom mobility is enhanced then formation of more nucleation centers can be expected. One way to enhance the ad-atom mobility is to increase the substrate temperature. However, with increase in substrate temperature, ad-atom mobility may increase to such an extent that it may result in formation of big clusters. Therefore while developing nanocrystalline film, it is essential to control the substrate temperature at an optimum value at which necessary amount of nucleation centers are created for uniform grain formation on all over the film surface, but the further grain agglomeration is restricted. [12].

In the present work thin films of CdTe are deposited at 573 K, 623 K, 673 K and 723 K. The role of substrate temperature in the process of nanocrystalline thin film formation is studied.

2. Experimental Method

Nanostructured thin films of 200 nm thickness were prepared by thermally evaporating 99.99% pure CdTe powder in vacuum of the order of 10^{-6} mbar. The deposition rate was maintained at 16 – 18 amp/s and the current was approximately 45 ampere for all the films. The thickness of the film was monitored in situ by quartz crystal thickness monitor and is of the order of 200 nm. The films of thickness of 200 nm were deposited at substrate temperatures of 573 K, 623 K, 673 K and 723 K respectively.

The structural characterization of these films is carried out using X-ray diffractometer (XRD) using Cu-Kα radiation of wavelength 1.5418 A^0 on Phillips Pananalytical Xpert Pro MPD spectrometer. The optical measurements are done by Varion CARRY 500 UV-vis spectrometer. The surface morphology of the thin films is carried out by ZEISS Scanning Electron Microscope (SEM).

3. Results

3.1 X-Ray Diffraction analysis

X-ray diffraction (XRD) studies are carried out to investigate structure of the films. Figure 1 shows XRD patterns of all the films deposited at substrate temperatures of 573 K, 623 K, 673 K and 723 K. The peak positions are observed at 2θ = 23.69^0, 39.36^o and 46.31^o. This indicates cubic nature of the films. [JCPDS data]. XRD results also indicate that the substrate temperature does not affect the orientation (111) of the films.

The crystallite size (D) is calculated using the Debye Scherrer formula [13].

$$D = \frac{0.94\,\lambda}{W\cos\theta} \tag{1}$$

The strain (ε) and dislocation density (δ) **[**14**]** are calculated using the formulae:

$$\varepsilon = \frac{W\cos\theta}{4} \tag{2}$$

$$\delta = \frac{1}{D^2} \tag{3}$$

The lattice parameter 'a' is evaluated from the relation

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (4)$$

The effect of substrate temperature on lattice constant, crystallite size, strain and dislocation density is listed in table no. 1.

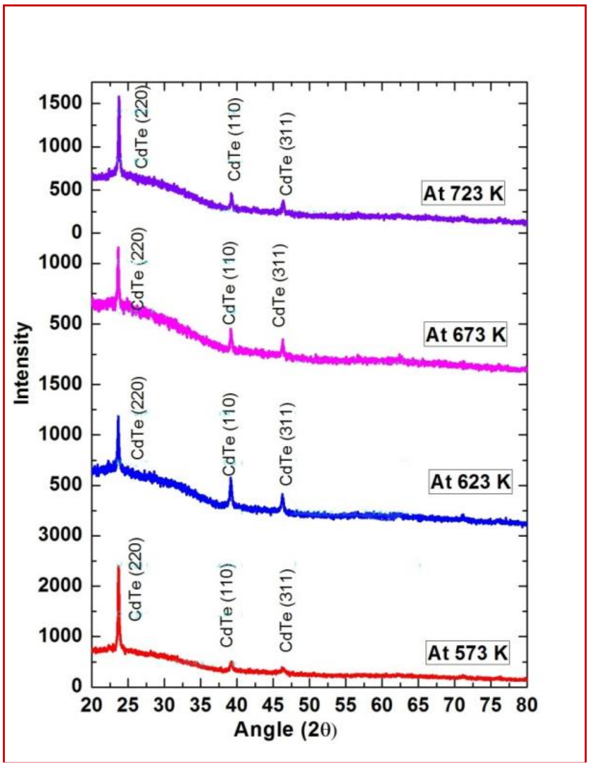

Fig. 1: XRD Pattern of the films deposited at substrate temperatures 573 K, 623 K, 673 K and 723 K

Table. 1 Effect of substrate temperature on lattice constant, crystallite size, strain and dislocation density

Substrate Temperature (K)	FWHM (degrees)	Lattice constant 'a' A^0	Crystallite size (nm)	Strain ε ($lin^{-2}m^{-4}$)× 10^{-2}	Dislocation density δ (lin/m^2) × 10^{14}
573	0.38	6.36	22	1.6	19.7
623	0.26	6.45	32	1.1	9.6
673	0.24	6.47	34	1.0	8.3
723	0.18	6.51	47	0.7	4.4

It is observed that the crystallite size changes with substrate temperature. The crystallite size (radius) increases from 22 nm to 47 nm with the increase of substrate temperature.

It is also observed that the microstrain decreases from 1.6×10^{-2} to 0.7×10^{-2} lin^{-2} m^{-4} with increase in substrate temperature. This decrease in microstrain with increase in substrate temperature may be attributed to the difference in the temperature coefficient of expansion of the glass substrate and CdTe thin films [15].

The lattice parameter values are calculated for all the films and are listed in table 1. The lattice parameter values are slightly different from reported bulk value of $6.48A^0$. The variation in the lattice constant can be attributed to decrease in the strain with increase in substrate temperature [16].

The dislocation density is a measure of the number of dislocations in a unit volume of a crystalline material **[14].** It is measured by the number of dislocation lines crossing per unit area. The dislocation density δ decreases from 19.75×10^{14} lin/m^2 to 4.40×10^{14} lin/m^2 with increase in substrate temperature. The decrease in both strain and dislocation density indicate that the film quality improves at elevated substrate temperatures. [17]

3.2 Scanning Electron Microscopy (SEM) studies

Effect of substrate temperature on the morphology of the CdTe films is investigated by SEM. Figure 2(a,b,c,d) shows SEM micrographs of the films grown at substrate temperatures 573 K, 623 K, 673 K and 723 K respectively. SEM micrographs exhibit the granular nature of all the films. No voids, pinholes, cracks, peeling etc. are seen on the surface. This indicates that the increase in substrate temperature does not affect the adherence of the film to the substrate.

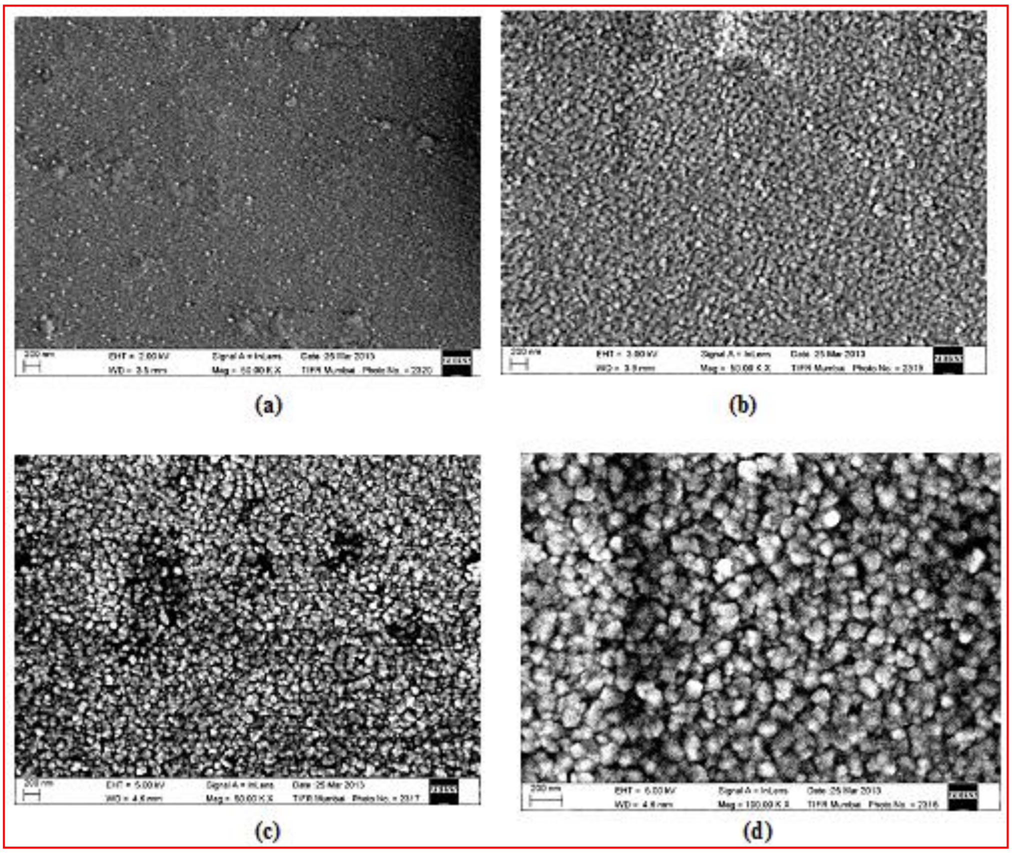

Fig. 2: SEM micrographs of films deposited at substrate temperatures (a) 573 K, (b) 623 K, (c) 673 K and (d) 723 K

In the SEM micrograph of film deposited at 573 K indicates formation of circular nanograins having diameter ~ 46 nm. However, these nanograins are not seen all over the surface. The grain size calculated using Debye Scherer formula indicates the grain size (radius) to be 22 nm. The grain size estimated on the basis of SEM and XRD studies match with each other.

When the substrate temperature is elevated to 623 K, formation of circular nanograins is seen all over the surface. The diameter of these grains is ~ 60 nm. In this film also the grain size matches with that of XRD results. When the substrate temperature is further elevated to 673 K and 723 K the grain diameter increases to ~ 103 nm and ~ 151 nm respectively.

At these temperatures of 673K and 723K the grain size estimated on the basis of SEM does not match with XRD results.

To our opinion, the reason behind this is as follows. The XRD technique estimates the crystallite size and SEM estimates the grain size. At substrate temperature of 573K and 623K single crystallite corresponds to single grain. Therefore the XRD results and SEM results match with other. However, at elevated substrate temperatures of 673K and 723K 2-3 crystallites must have agglomerated and formed one grain as seen in the corresponding SEM micrograph. Therefore the XRD and SEM results do not match with each other.

Table.2 Grain size by SEM and Crystallite size by XRD results for different substrate temperatures

Substrate Temperature (K)	XRD Results Crystallite Size (nm))	SEM Results Grain Diameter (nm)
573	22	46
623	32	60
673	34	103
723	47	151

3.3 UV-Vis absorption spectroscopy analysis

In the present investigation, optical absorption in CdTe thin films deposited at different substrate temperatures is studied in the wavelength range 300–1200 nm using Varion CARRY 500 UV-Vis photo spectrometer. The optical band gap values of the films were obtained from absorption measurements and by plotting $(\alpha h\nu)^2$ vs.hν. Figure.3 (a,b,c,d) shows a plot of '$(\alpha h\nu)^2$' versus energy hν for CdTe nanocrystalline thin films deposited at substrate temperatures 573 K, 623 K, 673 K and 723 K.

The values of energy band gap of the thin films as determined by extrapolation of linear portion of the plots $(\alpha h\nu)^2$against hν to the energy axis. The calculated band gap values are 2.47 eV, 2.44 eV, 2.28 eV and 2.20 eV for the films deposited at substrate temperatures of 573 K, 623 K, 673 K and 723 K respectively.

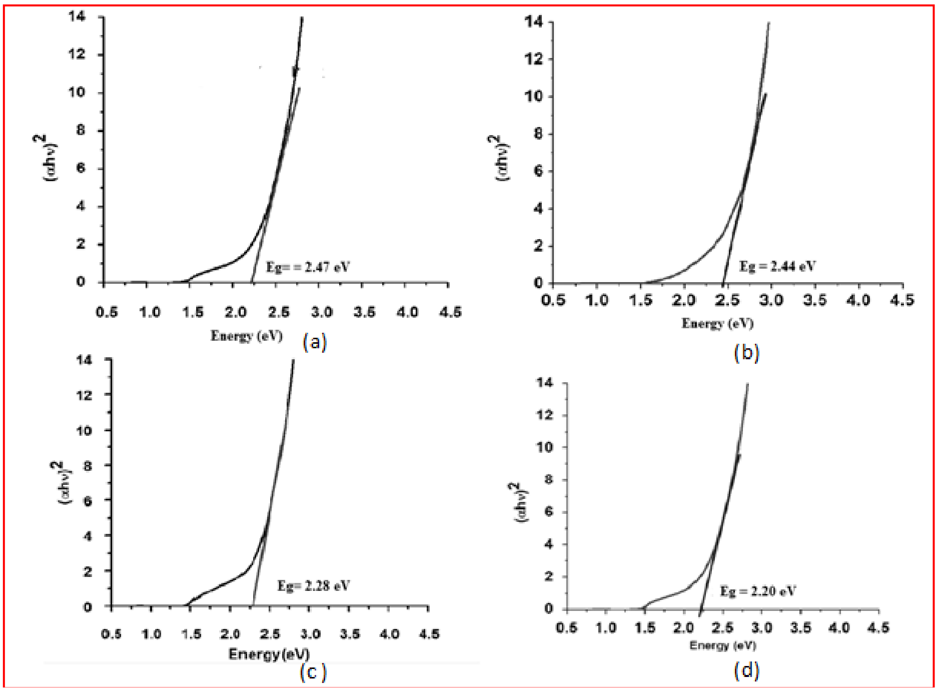

Fig. 3: Plot of '$(\alpha h\nu)^2$' versus energy hν (eV) of the films deposited at substrate temperatures (a) 573 K (b) 623 K (c) 673 K and (d) 723 K

The bandgap values evaluated for the films deposited at substrate temperatures 573 K, 623 K, 673 K and 723 K are listed in table no. 3. The bandgap of all the films is higher than the standard room temperature bulk material bandgap value i.e. 1.56 eV. The widening of bandgap is attributed to nanocrystailline nature of the films [18].

In semiconducting materials, when the grain size becomes comparable with exciton Bohr radius then due to quantum confinement effect the bandgap increases. When a CdTe film is deposited at 573 K temperature the radius of nanograin is ~ 22 nm which is comparable with exciton Bohr radius of CdTe i.e. 15 nm [19]. Hence a large bandgap increase of 0.91 eV is seen. However, as substrate temperature increases the grain size increases and therefore the bandgap change also decreases.

Table No.3 Effect of substrate temperature on band gap

Substrate Temperature (K)	Band gap energy (eV)	Increase in band gap (eV)
573	2.47	0.91
623	2.44	0.88
673	2.28	0.72
723	2.20	0.64

4. Discussion

In the present work, naocrystalline films of CdTe are deposited 573 K, 623 K, 673 K and 723 K. The experimental result indicates that the nanograin size and film morphology is strongly dependent on substrate temperature.

The observed substrate temperature dependent nanophase formation can be explained as follows. The substrate temperature is expected to affect mainly two parameters ; namely the ad-atom mobility on the surface and formation of nucleation centers [11].

The SEM results indicate that, at substrate temperature of 573 K the widely spaced circular nanograins of size (radius) ~ 23 nm are formed. The nanograin formation is observed only at certain areas of the substrate. During thermal evaporation the target material is evaporated and the target vapor ions impinge on the substrate. It can be said that this substrate temperature, the impinging ions got struck to the surface at the place where they landed. This reduced the surface diffusion of impinging ions and some part of the substrate was shielded for direct impingement of atoms. As a result, very few nucleation centers were formed and the grain growth was started. Due to low surface diffusion the grain growth was restricted and widely spaced nano grains of size 23 nm are observed. The nanograins size estimated on the basis of SEM is in accordance with that obtained from XRD results.

When the substrate temperature is further increased to 623 K, uniform monodispersed circular nanograins of diameter ~ 60 nm are formed as seen in SEM micrograph figure 2 (b).This observed nanograin formation can be attributed to increased ad-tom mobility which leads to the formation of more nucleation centers all over the surface. Due to the increased substrate temperature surface diffusion processes also enhance and atoms join together. Therefore slightly bigger nanograins are formed in comparison with the grains formed when substrate temperature was 573 K. Due to increase in particle size, the strain and dislocation density of the film decrease.

When the substrate temperature is further increased to 627 K and 723 K the ad-atom mobility further increases. At these substrate temperatures the formation of a larger grain size is favored due to increased surface diffusion and ad-atom mobility. This leads to agglomeration of grains. Thus in the SEM micrograph larger grains of diameter ~ 103 nm and 150 nm are observed.

5. Conclusion

Nanocrystalline CdTe thin films are deposited by thermal evaporation method at substrate temperatures of 573 K, 623 K, 673 K and 723 K. X-ray Diffraction (XRD) studies indicate that all the nanocrystalline CdTe thin films had a cubic structure with a preferred orientation along the (111) direction irrespective of the substrate temperature. The crystallite size (radius) calculated on the basis of XRD results is found to be 22 nm, 32 nm, 34 nm and 47 nm for the films deposited at substrate temperatures of 573 K, 623 K , 673 K and 723 K respectively. The bandgap values calculated using Uv-Vis spectroscopy reveal that the bandgap is widened in all the films due to their nanocrystalline nature.

Scanning Electron Microscopy (SEM) studies indicate formation of monodispersed nanograins at substrate temperature of 623K. At substrate temperature of 573K some part of the substrate is shielded for grain formation and at substrate temperature of 673K and 723K the gains agglomerate.

Our experimental results indicate that when the substrate temperature is 623K the ad-atom mobility and the surface diffusion processes are balanced in such a way that the uniform monodisperse circular nanograins of diameter ~ 60 nm are formed all over the surface.

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