

Influence of CdCl₂ Treatment Temperature on Structural and Optical Properties of CdTe Thin Films

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Abstract—In this work the influence of the CdCl₂ treatment temperature on the structural, morphological, and optical properties of CdTe thin films were investigated. The CdTe films were grown on CdS coated borosilicate glass by Close-Spaced Sublimation (CSS) technique using a standard recipe. The CdS coating was done by RF sputtering. The deposited CdTe films were treated with aqueous CdCl₂ solution of 0.3 M molar concentration at 380°C, 385°C, 390°C, 395°C and 400°C for 25 minutes each. All the treated films show polycrystalline nature with intense peak at (111) orientation. The highest prominent peak and the largest crystallite size were found for 395°C treatment temperature. The SEM study confirms that the film treated at 395°C temperature is compact and shows uniform surface morphology. Sharp transmittance edges are found at 830 nm wavelength for all treated films which also signifies the higher crystallinity, suitable for high performance CdTe solar cell application.

Keywords—CdTe thin film, Close-spaced sublimation, CdCl₂ treatment, XRD, SEM, UV-Vis, Solar cells.

I. INTRODUCTION

The polycrystalline CdTe lies in the group of most potential photovoltaic (PV) chalcogenide materials that have been extensively studied in the last few decades. It possesses unique physical properties which make itself an ideal p-type absorber material for CdTe thin film (TF) based solar cells. It has a 1.45 eV direct bandgap which is near optimum for PV energy conversion from solar radiation. Its absorption coefficient is inherently over $5 \times 10^5 \text{ cm}^{-1}$ at the effective wavelengths of sun radiation [1]. Moreover, among all the semiconductors of II-VI group the CdTe has the largest lattice constant and lowest negative formation enthalpy. All the above mentioned properties along with the lower cost possibility, long-term stability, and higher energy conversion efficiency have made the CdTe absorber material superior than its counterparts.

A wide assortment of deposition methods, for example, electro-deposition, vacuum deposition, MOCVD, spray pyrolysis, MBE, screen printing, RF sputtering, closed-space sublimation (CSS) have been deployed for fabrication

of CdTe thin films [2]. Although each of these techniques is effective in the deposition of high quality film, solar cells with highest efficiencies have been reported to have CdTe films grown by the CSS technique [3]–[5]. The CdTe TF solar cells have already crossed the benchmark of 22% photovoltaic conversion efficiency at research level and 18% efficiency at module level [6]. This pv conversion efficiency depends upon the electrical, optical and most importantly structural properties of the CdTe absorber layer. The results obtained from numerous studies have confirmed that CdCl₂ treatment facilitates recrystallization as well as grain-growth inside the CdTe TFs which further improve these properties [7], [8]. As a result, the CdCl₂ treatment is considered as one of the most crucial steps in the fabrication of high quality CdTe thin films for solar cell application.

This treatment can be carried out by both dry and wet processes. The wet CdCl₂ treatment is widely used by the researchers because it is simple and easy. In this process the CdTe thin film is dipped into a CdCl₂ solution of about 0.3 M molar concentration for a small time duration and subsequently annealed at high temperature for 10 to 40 minutes [9]–[12]. There is a large ambiguity among the researchers about the CdCl₂ treatment temperature. In the literature, many treatment temperatures in the range of 350 to 400°C have been found [9]–[14]. Moreover, it is not concluded yet that, how various film properties get influenced by the CdCl₂ treatment temperature.

The main focus in this work is given on the effects of CdCl₂ treatment temperature on the structural and optical properties and surface morphology of the CdTe thin films. The CdTe films were deposited using CSS technique. The deposited CdTe films were treated with CdCl₂ solution of 0.3 M molar concentration for 25 minutes at varying temperatures from 380°C to 400°C at steps of 5°C. The structural and optical properties and surface morphology of the CdTe films were studied using XRD, UV-Vis and SEM respectively.

II. EXPERIMENT

The borosilicate glass (30 mm × 30 mm × 1.5 mm) was used as the substrate because of its superior optical transmittance and greater strain point compared to the soda-lime glasses [15]. At first a scratched mark was drawn on one side of each substrate using a diamond pen cutter to distinguish between two sides of the substrates. Afterwards, both sides were mechanically scribed with a clean brush in a jar containing acetone for two minutes each side. The substrates were then rinsed with deionized (DI) water. This process was repeated for three times to ensure that no wax was remaining on the substrates. After being scribed, the substrates underwent through the standard 4-step methanol-acetone-methanol-deionized water (MAMD) [15] ultrasonic cleaning process. Each step of MAMD lasted for 15 minutes at 50°C temperature to make sure that the substrates were degreased properly. The wet substrate were dried by N₂ gas and then air baked at 100°C on a hot plate for 5 minutes.

A CdS thin film of 100 nm thickness was sputtered on the unscratched side of each cleaned substrate from a CdS sputtering target of 4N purity (99.99%), 2-inch diameter and 0.25-inch thickness. A NSC-3500 2-gun RF magnetron sputtering machine from Nano Master Inc. was used for sputtering the CdS thin films. During sputtering the Ar gas flow-rate to the sputtering chamber was maintained at 16 sccm and a constant 30 W RF power was applied to the plasma gun. The target was placed 7 cm below the substrate. The sputtering was continued for 30 minutes at 100°C substrate temperature. The thickness data of the sputtered CdS films was collected from the Quartz Crystal Monitor (QCM). A vacuum desiccator was used to store the CdS films to avoid any deterioration of the film quality that might be caused by staying in contact with the environment. After that CdTe thin films were deposited on the CdS films by close-spaced sublimation (CSS) technique.

The deposition of CdTe films by CSS is a one-by-one process meaning that only one film can be deposited at a time. CdTe powder of 99.99% purity was used as the CSS source material. A graphite susceptor of 2.85 cm was used as the both the source and substrate holder. The 0.6 cm deep susceptor was filled with the source powder which was then compacted with a glass slider. This compacted source powder was then sintered in an Argon ambient at 700°C for 30 minutes inside the quartz CSS chamber to form a hard source of CdTe material. Prior to the deposition, the CSS chamber was brought to a vacuum level of 10 mTorr by using a rough pump and then purged with pure N₂ gas to remove all moisture and foreign particles. The deposition was done at source and substrate temperature of 650°C and 620°C respectively in Ar ambient which was found in [15]. The heating was accomplished by incorporating two tungsten-halogen bulbs of 2 kW rating into the system, one placed at the top and the other at the bottom of the chamber. The process pressure was monitored by a pressure gauge and maintained manually at 1.5 Torr by controlling a throttle

valve. The deposition of each CdTe film was carried out for 10 minutes.

At the end of the deposition of CdTe films, a CdCl₂ solution of 0.3 M molar concentration was prepared by diluting CdCl₂ powder of 99.99% purity in DI water. The deposited CdTe films were then dipped into this solution for 30 seconds and then dried in air by a hand blower. Afterwards, five CdTe samples were annealed at 380°C, 385°C, 390°C, 395°C and 400°C respectively for 25 minutes in a furnace. During annealing of the samples the vacuum level of the furnace was maintained at 100 mTorr by using a rough pump. After annealing, the samples were kept inside the chamber for natural cooling. The treated samples were brought out after the chamber came back to room temperature and then washed with moderately hot DI water for 1 minute so that no leftover CdCl₂ remains on the samples.

The structural properties of both as-grown and treated CdTe films were investigated from the XRD spectras obtained in the 2-Theta domain ranging from 15° to 80°. A diffractometer manufactured by RIGAKU company was used to obtain the XRD patterns using the Cu-K α X-ray radiation ($\lambda = 0.15408$ nm). The lattice constant and lattice type, the crystallite size, dislocation density, and micro-strain were determined from these XRD patterns. The morphology of treated films at 390°C and 395°C were explored by JSM-7600F FESEM. The grain growth and film uniformity were observed from the images. The SHIMADZU UV-2600, UV-Vis spectrophotometer was used to obtain the optical transmittance of the CdTe films in the 220 nm to 1400 nm wavelength range.

III. RESULTS AND DISCUSSION

A. Structural Analysis

The XRD patterns of the as-grown and CdCl₂ treated CdTe thin films at various annealing temperatures were investigated to find the influence of the treatment temperature on the structural property of the films. The XRD patterns are presented in Fig.1. It becomes apparent that all the samples exhibit a dominant peak at $2\theta = 23.67^\circ$ corresponding to the (111) cubic plane of the CdTe material. The XRD spectra of the untreated CdTe film has five more peaks with significantly lower intensity at $2\theta = 39.24^\circ, 46.4^\circ, 56.81^\circ, 71.17^\circ$ and 76.21° which corresponds to the (220), (311), (400), (422) and (511) cubic planes respectively. It confirms that all the deposited films are polycrystalline and zincblende structured with strong preferential orientation along the (111) cubic plane. The XRD patterns of the CdCl₂ treated films at low temperatures also contain several small peaks like the as-deposited film. As the CdCl₂ treatment temperature increases the comparatively smaller peaks start to disappear. On the contrary the prominent peak intensity from (111) plane increases. It indicates that the crystallinity and grain orientation of the films improves with the increasing CdCl₂ treatment temperature.

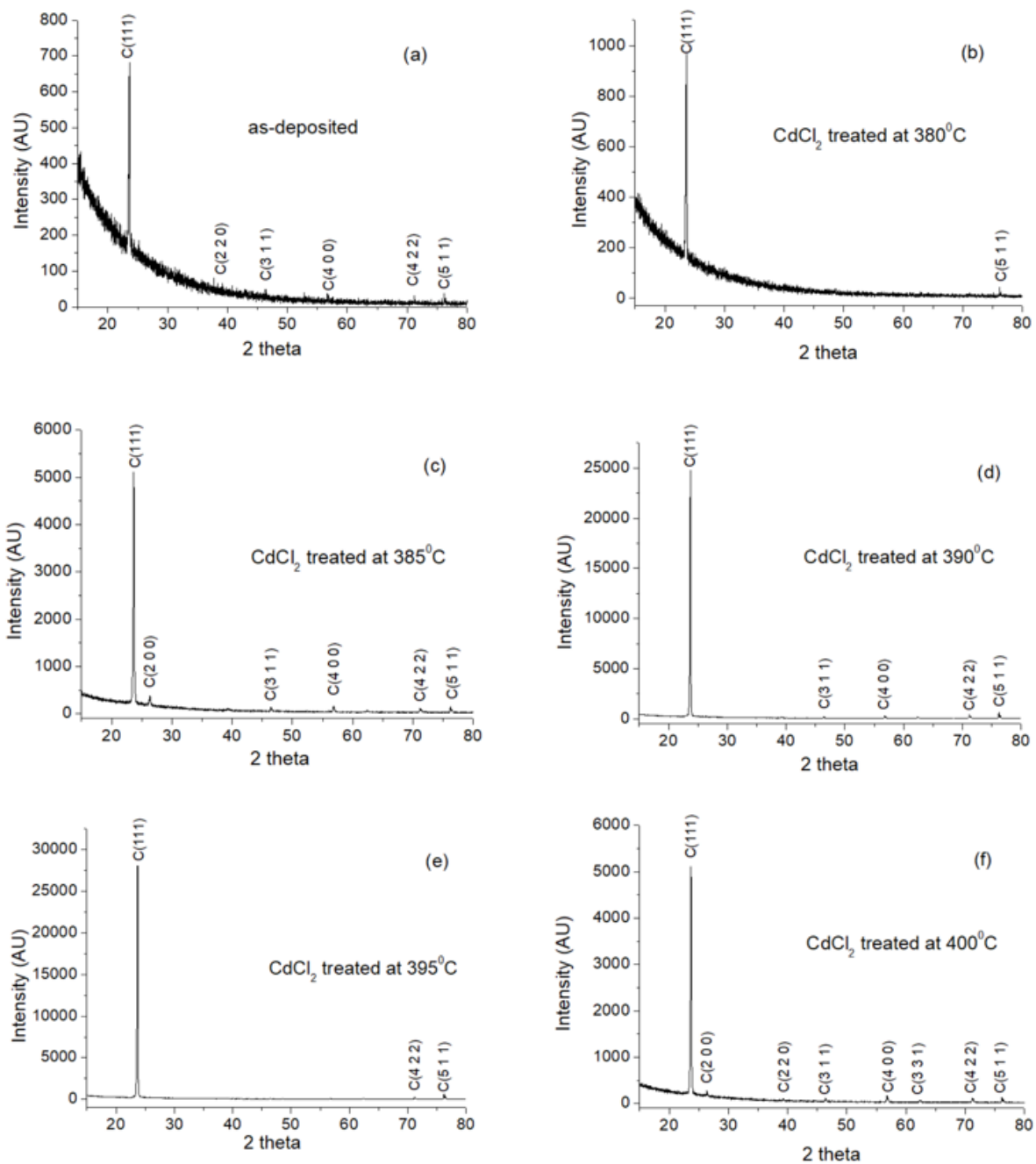


Fig.1. XRD pattern of (a) as-deposited and CdCl₂ treated CdTe thin films at (b) 380°C (c) 385°C (d) 390°C (e) 395°C and (f) 400°C treatment temperature

The CdTe film treated at 395°C shows the highest peak intensity along the (111) orientation. Besides this, in the XRD pattern only two other small peaks from (422) and (511) planes persist whereas all other peaks disappear. This indicates that the CdTe thin film treated at 395°C possesses the best crystalline property and grain-growth along the (111) preferential orientation. When the CdCl₂ treatment temperature is further increased beyond 395°C, the prominent peak intensity decreases rapidly. In addition to this, all other peaks of the as-deposited film reappear. These two facts confirm a deterioration of the crystallinity and grain-growth orientation of the CdTe thin films treated with CdCl₂ at more than 395°C.

In order to get better understanding of the effects of CdCl₂ treatment temperature on the grain orientation of CdTe thin films Fig.2 is drawn. Fig. 2 shows the variation of prominent peak intensity from (111) plane with respect to the treatment temperature. It is conspicuous that treatment temperatures below 390°C provides weak recrystallization. However the treatment temperature of 390°C and 395°C provides enough thermal stress for recrystallization. The best recrystallization occurs at 395°C. Annealing at 400°C causes over thermal stress as a result of which crystallinity of the film decreases roughly with 5 times less intense (111) peak compared to that of 395°C sample.

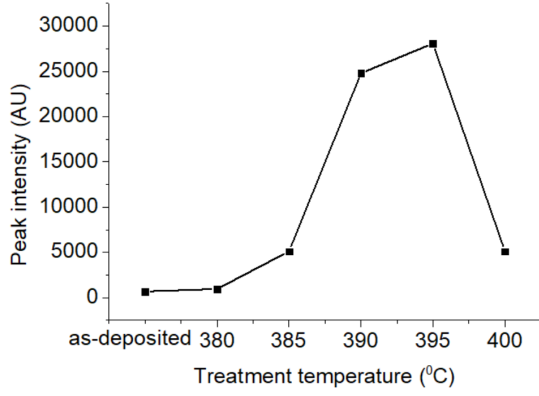


Fig. 2. Peak intensity from (111) plane versus CdCl₂ treatment temperature

For a more detail analysis of variation in the structural property with the treatment temperature lattice constant, crystallite size, dislocation density, and micro-strain have been calculated from the peaks of XRD patterns. The lattice constant 'a' of the cubic structured CdTe thin films is determined using Brag's law and Vegard's law [16].

$$d_{hkl} = \frac{\lambda}{2} \times \cos ec(\theta) \quad (1)$$

$$a_{cubic} = d_{hkl} \times (h^2 + k^2 + l^2)^{0.5} \quad (2)$$

Where, λ represents the wavelength of the X-ray radiation (Cu-K α) equal to 0.15408 nm, d is called the interplanar spacing in the lattice and θ refers to the angle in radian measured between the incident X-ray and scattering crystallographic planes. The crystallite size D , micro-strain ϵ , and dislocation density δ are calculated using Debye-Scherrer formula [16].

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos(\theta)} \quad (3)$$

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

$$\delta = \frac{15\epsilon}{\alpha D} \quad (5)$$

Where, β refers to the Full-Width at Half Maxima (FWHM) of the diffraction peaks. The λ and θ have their usual meaning.

Fig. 3 presents the variation of crystallite size of the CdTe films with the treatment temperature. As seen in the figure, the crystallite size increases with the treatment temperature. This is because, at high temperature the CdCl₂ sintering flux causes the consolidation of smaller grains into larger ones and increases the crystallite size. The largest crystallite size is observed in the sample treated at 395°C. However, at 400°C a drastic decrease in crystallite size from 68 nm to 45 nm is observed presumably due to the over thermal stress induced in the film.

The variation of lattice micro-strain with the treatment temperature is exhibited in Fig. 4. In the crystal, micro-strain is developed when atoms are displaced from their actual

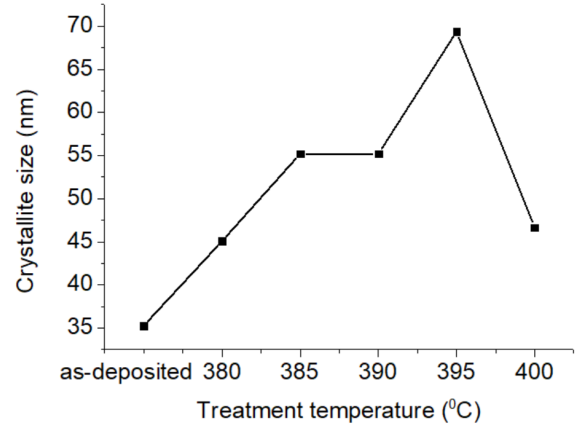


Fig. 3. Crystallite size versus CdCl₂ treatment temperature

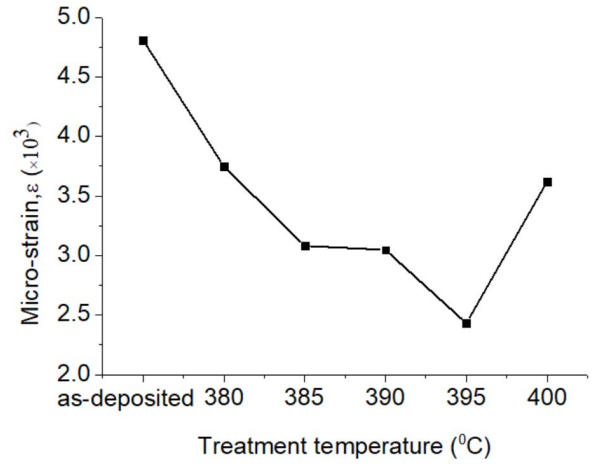


Fig. 4. Micro-strain versus CdCl₂ treatment temperature

lattice positions. This phenomena is associated with the lattice 'misfit' and is influenced by the growing conditions of the films. It is found that the micro-strain is maximum in the as-deposited film. It follows a decreasing trend with the increasing CdCl₂ treatment temperature till 395°C. However, it increases with treatment temperature beyond 395°C

Dislocation is a crystal imperfection resulting from the relative difference between the registries of lattice points at different parts of the crystal. Like the micro-strain, dislocation density is higher in the samples treated at lower temperature and decreases with the increased treatment temperature as shown in Fig. 5. It reaches the minimum

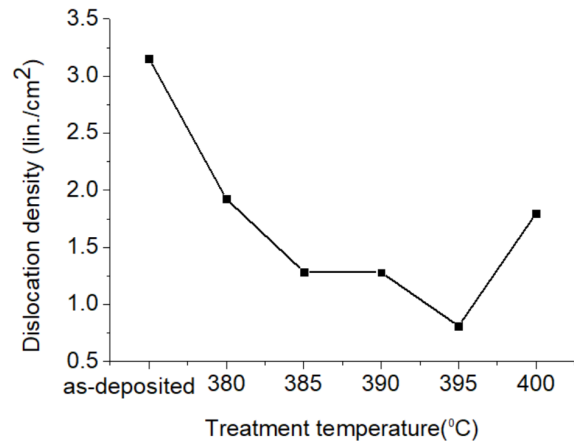


Fig. 5. Dislocation density versus CdCl₂ treatment temperature

value at 395°C treatment temperature and increases afterwards. The results of the above analysis along with the calculated values of lattice constant of all the samples are presented in TABLE I. The calculated values of lattice constant of the as-deposited and CdCl₂ treated films are almost equal to the standard lattice constant value (6.48 Å) of CdTe powder material which confirms that the deposited films are of CdTe material. The subtle increase in the calculated lattice constant is due to compressive stress. Since the temperature variation between samples is only 5°C, therefore the change in lattice constant with temperature is less consistent. May be, the treatment effect in crystallite size is significant and suggesting 395°C is a critical temperature for attaining good optoelectronic quality CdTe film. This should effect the electronic transport and bandgap of the films.

TABLE I. STRUCTURAL PROPERTIES OF CdTe THIN FILMS

Treatment temperature (°C)	Crystallite Size (nm)	Micro Strain, ϵ ($\times 10^3$)	Lattice Constant, a (Å)	Dislocation Density δ ($\times 10^{11}$ cm ⁻²)
As-deposited	35.27	4.81	6.52	3.15
380	45.08	3.75	6.50	1.92
385	55.19	3.07	6.52	1.29
390	55.20	3.06	6.49	1.28
395	69.35	2.43	6.49	0.81
400	46.63	3.62	6.50	1.79

B. Optical Analysis

The optical transmittance spectra of as-deposited and CdCl₂ treated CdTe films were investigated by SIMADZU UV-2600 spectrophotometer for wavelengths of the range 220 nm to 1400 nm. In Fig. 6, a sharp transmission edge is found for all the films which assures the higher crystallinity of the as deposited and treated films. The transmittance in the visible wavelength region approaches to zero which signifies that the films are suitable to be used in solar cell as an absorber material. Moreover, the transmittance of the CdTe films decrease inversely with treatment temperature in the higher wavelength region as shown in the figure.

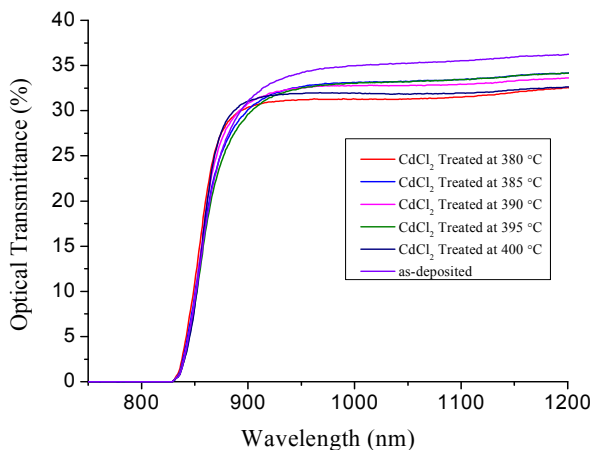
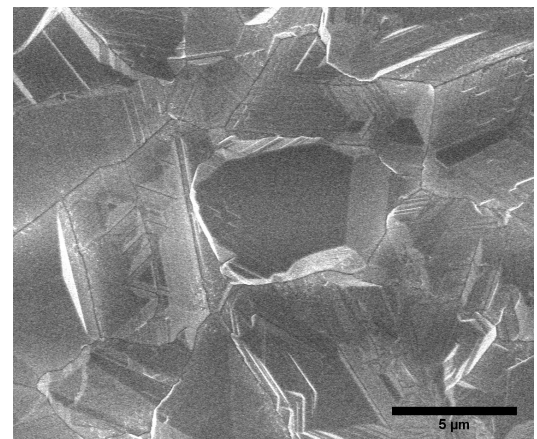


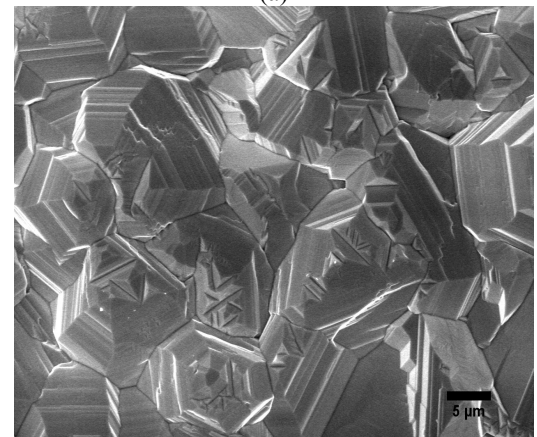
Fig. 6. Optical transmittance of the as-deposited and CdCl₂ treated CdTe films versus treatment temperature

C. Surface Morphology

From the above analysis the better structural and optical properties are found for 395°C and 390°C treatment temperatures respectively compared to other temperatures. The surface morphology of the CdTe films treated at these two temperatures were investigated by JSM-7600F Schottky Field Emission Scanning Electron Microscope (FESEM) and the micrographs are presented in Fig. 7. The average grain size estimated are 7 ± 2 μ m and 15 ± 2 μ m for 390°C and 395°C respectively. It is really intriguing to observe more than two times increase in grain size just by 5°C increase in treatment temperature. It is observed that the films are very compact and uniformly deposited. In addition, no void and cracks are found in the micrographs. However, the better compactness and surface uniformity are found for 395°C treatment temperature.



(a)



(b)

Fig. 7. SEM image of CdCl₂ treated CdTe thin films at (a) 390°C and (b) 395°C

IV. CONCLUSION

The paper summarizes the effect of CdCl₂ treatment temperature on microstructural, Optical and morphological properties of CdTe thin films. The XRD spectra revealed that all the films have desired polycrystalline nature and the preferential intense peak along the (111) cubic plane. The crystallite size as well as the peak intensity of the treated films are found to increase with treatment temperature and reach a maximum value at 395°C beyond which the grain size falls due to the developed micro-strain and crystal imperfection. SEM micrograph also confirms the

compactness of grain growth and uniformity of the treated films. Optical transmission spectra shows that the films completely absorb the visible wavelength and a sharp transition occurs at the edge of 830 nm wavelength which is good enough for CdTe solar cell application. All the achieved properties of CdCl₂ treated CdTe thin film at 395°C as mentioned above confirm their potentiality to be exploited as the absorber layer in high performance CdTe solar cells.

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