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Effect of $CdCl_2$/annealing on the crystalline transformation of CdTe thin films grown by evaporation at a low substrate temperature

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Abstract

The structural and optical properties of CdTe thin films prepared at a low substrate temperature were investigated before and after the $CdCl_2$/annealing. The crystal structure of CdTe film was cubic with a strong (111) preferential orientation. Annealing at 400 °C without $CdCl_2$ treatment results in a decrease in the (111) peak intensity while the intensities of the (220), (311) and (331) peaks appeared, indicating that the texture is significantly changed. However, after the $CdCl_2$/annealing, the film exhibited a hexagonal phase as a dominant structure. The scanning electron microscopy patterns showed that the as-deposited and annealed samples had almost the same grain size. However, the grain size of the sample annealed after the $CdCl_2$ treatment increased significantly. The optical band gap values for the as grown and $CdCl_2$/annealed films were determined to be $\sim$1.48 eV and $\sim$1.49 eV, respectively.

Key Words: Thin films, vacuum deposition, electron diffraction, crystal structure

1. Introduction

Cadmium telluride is one of the most promising polycrystalline materials for thin film solar cells due to its some physical properties: (i) it has a direct band gap (approximately 1.5 eV at room temperature), (ii) it has a high absorption coefficient (larger than 10^5 cm^{-1} at wavelengths around 700 nm), (iii) it can be obtained as p-type. It is known that cadmium telluride, like other II-VI compounds, can exist in both the cubic (ZB) and hexagonal (WZ) crystal structures and the energy difference between these two phases is small [1]. For this reason, it is difficult to grow pure single phase films for CdX (X = S, Se, Te) compounds. However, it is possible to stabilize the preferred phase to dominate the film by choosing appropriate growth and control techniques.

For the case of CdTe, the equilibrium cubic phase is relatively well known compared to its hexagonal phase which is poorly understood because it is metastable and difficult to produce in pure form [2]. The expected changes regarding optoelectronic properties in the hexagonal CdTe phase, such as a band gap broadening, together with the fact of a better matching with hexagonal CdS window layer in CdTe based solar cells, may be an important stage to increase solar cell based CdTe performance.

Aramoto et al [3] have reported on a CdTe/CdS solar cell with an efficiency of 16%. Some of the commonly used low cost growth techniques for CdTe thin film production include electrodeposition [4], spray pyrolysis [5] and close-spaced sublimation [6]. Irrespective of the growth process, the grain size and surface morphology of CdTe films are two of the important parameters that affect the performance of active devices such as solar cells made on such layers. For example, fabrication of high efficiency solar cells requires films with columnar grains to minimize grain boundary crossings by light generated minority carriers. Therefore, understanding the microstructure and morphology evolution in polycrystalline CdTe films is important to further develop an understanding of the performance of devices employing these layers. Polycrystalline films are used in a wide variety of applications in which their average grain size, distribution of grain size and distribution of grain orientations affect their performance and reliability. These grain structure characteristics are often defined by grain formation and growth during the film formation period. However, they may also be modulated through post-deposition process steps involving high temperature annealing [7–8].

Interest in the properties of CdTe films grown at low temperatures has increased in recent years due to their various device applications [9–14]. It is known that the grain boundaries in polycrystalline CdTe thin films have a direct influence on the electrical properties of the device. One of the critical stages in the device fabrication is the treatment of the CdTe film, after application of the $CdCl_2$ layer on the surface: a process that is essential in the production of high-efficiency CdS/CdTe cells [15]. In this work, we produced CdTe thin films on the glass substrates at -73 °C (liquid nitrogen cooled) and then annealed the films at 400 °C treated with and without $CdCl_2$. Effects of growth and post-deposition annealing on the film properties such as stabilization of crystal structure, grain size, texture, and optical band gap were studied to see if there was any correlation between these parameters.

2. Experimental

CdTe thin films were deposited by vacuum evaporation at a vacuum level of 3×10^{-2} Pa in a quasi-closed volume on glass substrates cooled by liquid nitrogen [16–18]. The films were grown at substrate temperatures of -73 °C using a CdTe powder source. The growth rate was $\sim$5 nm/s and the final thickness of the film determined from the transmittance interference pattern was found to be in the range of 2–3 μm. These films were annealed before and after $CdCl_2$ treatment at 400 °C for 30 min. The $CdCl_2$ layer was deposited on CdTe film surface using a saturated solution of $CdCl_2$ in boiling methanol for 5 min. After the application of the solution on the film surfaces, the films were heated at 400 °C for 30 min in air. CdTe thin films obtained were investigated for structural and optical properties. X-ray diffraction (XRD) data was collected using a Rigaku D/Max-IIIC diffractometer with CuK_α radiation over the range of $2\theta = 20$–70° at room temperature. The morphological information was obtained by a JOEL JSM-6400 scanning electron microscope (SEM). The absorption spectra of the films were measured by Perkin-Elmer Lambda 2SUV/Vis Spectrometer with 190–1100 nm wavelength range using non-polarized light.

3. Results and discussion

Figure 1(a–c) show the X-ray diffraction spectra of CdTe thin films produced; as deposited on the cooled substrate at -73 °C, annealed at 400 °C for 30 min in air without $CdCl_2$ treatment and treated with $CdCl_2$ and annealed at 400 °C for 30 min in air, respectively. X-ray diffraction studies showed that the as-deposited film is polycrystalline in nature and belongs to the cubic phase with a strong preferred orientation along the (111) direction together with a small peak due to Te precipitate at $2\theta = 21.48°$ (Figure 1(a)). The appearance of this additional small peak is consistent with the one in PDF 00-023-1000. Annealing at 400 °C results in a decrease in the (111) peak intensity while the intensities of the (220), (311) and (331) peaks appeared. This is an indication of certain degree of randomization in the film texture with annealing which results from the preferential growth of (220), (311) and (331) grains in expense of (111) grain. The (111) peak positions for the as-deposited film and the film annealed at 400 °C are $2\theta = 23.80°$ and $23.72°$, respectively corresponding to

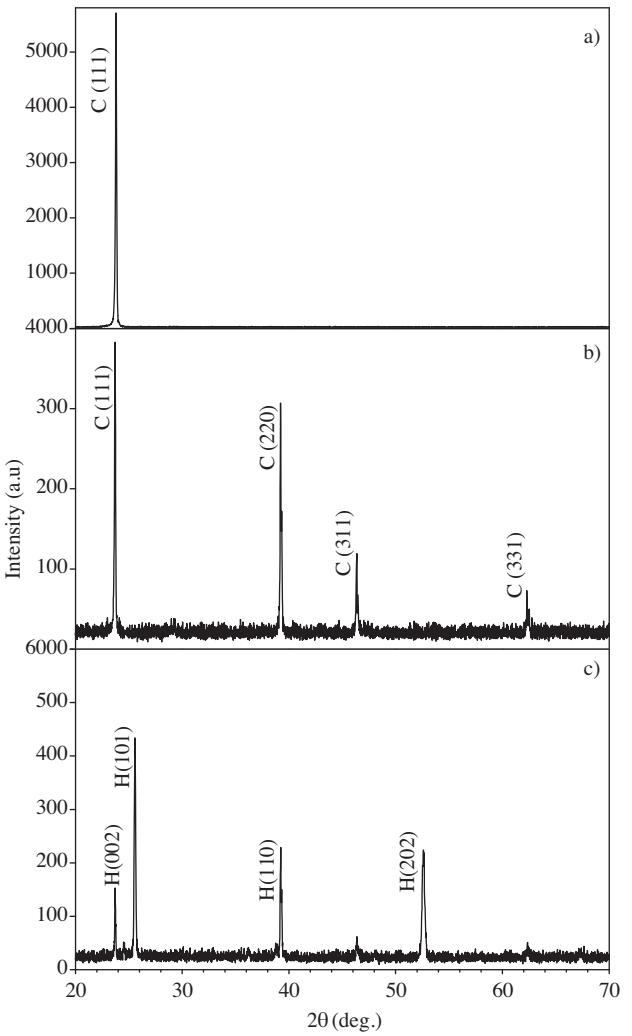


Figure 1. XRD diffraction spectra of CdTe thin films for (a) the as-deposited on the cooled substrate at -73 °C, (b) annealed at 400 °C for 30 min in air and (c) treated with $CdCl_2$ and annealed at 400 °C for 30 min in air.

lattice parameter values of 0.647 nm and 0.649 nm. The values of lattice parameters for the films are consistent with that of a powder sample (0.648 nm) [19]. The full width at half maximum (FWHM) of the cubic (111) peaks were calculated from the data of Figure 1(a,b). It was found that the FWHM decreased from 0.170° to 0.153° as the sample annealed at 400 °C. This may indicate a slight improvement of the crystalline nature of the film upon annealing while the structure remains still cubic. However, the peak due to Te precipitate disappeared upon annealing.

On the contrary, the X-ray diffraction data of the sample treated with $CdCl_2$ and annealed at 400 °C for 30 min in air (Figure 1(c)) shows a completely different pattern, indicating that the hexagonal phase appears predominately in the pattern of the sample. However, some small peaks such as (311) and (331) related to cubic phase are not disappeared entirely, meaning that cubic phase with a small amount still exists in the sample. The diffraction lines at 23.72°, 25.58°, 39.24° and 52.58° are related with the (002), (101), (110) and (202) planes of the crystalline CdTe hexagonal phase, respectively. Due to the proximity of peaks (111) and (220) to the peak positions of (002) and (110), it is rather difficult to differentiate the cubic structure from the hexagonal one. In our study, the interplaner distances for (111) and (002) were found to be 0.374 nm and 0.375 nm, respectively. These values are almost the same as those for CdTe in the literature [20-22].

The literature contains several reports about the phase purity of the CdTe films produced by different techniques. It is reported that, like other CdX (X = S, Se) compounds, CdTe can exits in both cubic and hexagonal structures, leading to different electronic properties. Thus, it is important to grow thin films with a pure phase (either cubic or hexagonal) to obtain stable and better device performance. Lalitha et al. [23] reported an XRD spectrum for the as-grown CdTe film consisting of peaks due to the cubic and hexagonal phases whereas the $CdCl_2$-treated CdTe films presenting only cubic with a (111) preferred orientation, which is entirely different from our results. The work of Li et al. [10] showed that their films deposited at room temperature contained both the cubic and hexagonal phases. But, the $CdCl_2$ treatment had created no substantial change in the phase constituents. However, the work by Rusu et al. [13] showed that the films produced at room temperature had only cubic phase and the post annealing at 350 °C left the sample still at cubic phase. It should be noted that the CdTe thin films used in our study are produced at a lower substrate temperature -73 °C compared with those mentioned above. The appearance of a small Te peak in Figure 1(a), namely the existence of small Te precipitate might interact with $CdCl_2$ during the annealing process, thus causing an unstable hexagonal form for CdTe. However, when the sample containing this unstable hexagonal phase etched in brom methanol, the surface returned to the original stable cubic phase removing the unstable hexagonal phase completely.

The band gaps obtained from the transmission optical spectra were determined from the plots $(\alpha h\nu)^2$ against $h\nu$. Figure 2 shows the extrapolated band gap values for the as-deposited, without and with $CdCl_2$/annealed films as ∼1.48, ∼1.48 and ∼1.49 eV, respectively. As can be seen from these data, the E_g values of the as-deposited film and the heat treated film without $CdCl_2$ are the same, but it is worth nothing the sharpening of the absorption edge upon annealing. However, the $CdCl_2$/annealing caused a slight change in the band gap value approaching to ∼1.49 eV. The difference is within the experimental error in the method used.

Figure 3 shows the surface SEM patterns of films deposited at substrate temperature of -73 °C and then annealed without and with $CdCl_2$ at 400 °C, respectively. As can be seen from these data, the grain size did not changed significantly upon annealing without using $CdCl_2$ but now contain voids around the grain boundaries. On the contrary, the grain size in the sample treated with $CdCl_2$ increased significantly.

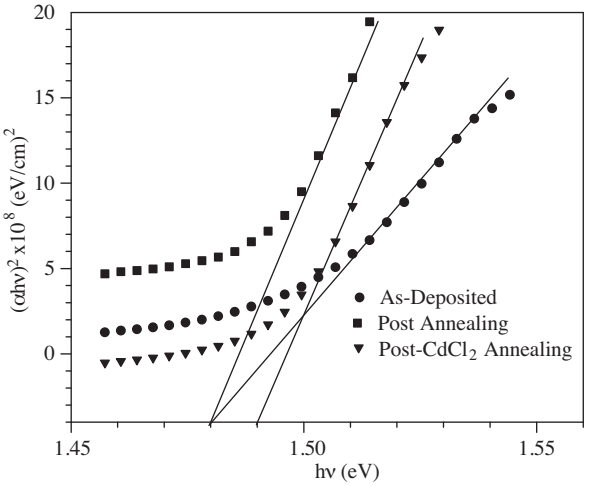


Figure 2. Absorption spectra of CdTe thin films deposited at -73 °C and annealed at 400 °C for 30 min in air with and without $CdCl_2$/annealing treatment.

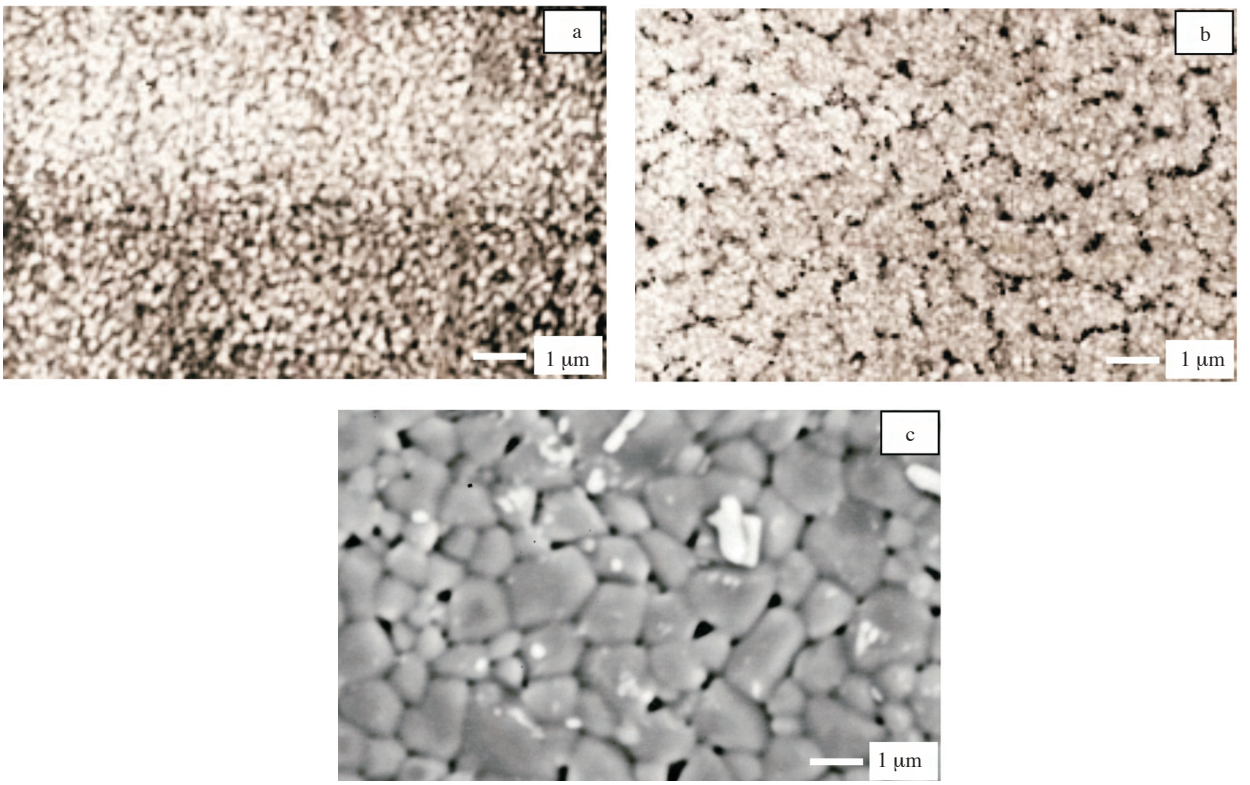


Figure 3. SEM images of films for (a) the as-deposited at a substrate temperature of -73 °C, (b) the annealed at 400 °C for 30 min in air and (c) treated with $CdCl_2$ and annealed at 400 °C for 30 min in air.

4. Conclusions

The XRD patterns reveal that the as-grown and annealed CdTe films were cubic. The texture is changed from the fully (111) preferred orientation to a certain degree of randomization upon annealing. After the

$CdCl_2$/annealing, the sample is transformed into a mixture of hexagonal and cubic phases; the hexagonal phase being predominant phase. The grain size increased for the $CdCl_2$/annealed film. The optical band gap values for the as-grown and $CdCl_2$/annealed films were found to be $\sim$1.48 eV and $\sim$1.49 eV, respectively.

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