

Microstructure of evaporated or sputtered CdTe films in relation to heat treatment

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We prepared 1- μm -thick CdTe films by thermal evaporation or radio frequency magnetron sputtering. The film deposition was conducted at various substrate temperatures (T_s), and sputtered films were post-annealed in air or vacuum. The CdTe films deposited by evaporation had larger grain sizes than the films deposited by sputtering, likely because the bombardment of high-energy particles during sputtering disturbed the crystallization of the film. The sputtered film was amorphous when grown at room temperature (RT), but crystalline when the T_s was increased during deposition. In case of the evaporated films, the preferred orientation was C-(111) when the T_s was at RT. However, when the T_s was increased, the intensity of the X-ray diffraction peak of C-(111) decreased and that of the C-(220) and C-(311) peaks increased. Finally, sputtered films grown at RT were treated with a post-annealing step at various temperatures. After this treatment, there was no significant difference in the grain size and XRD patterns of the films, likely because the maximum annealing temperature, 400 °C, was insufficient to change the microstructure of the film.

Key words: CdTe, Sputtering, Thermal evaporation, Heat treatment.

Introduction

Recently, many researchers have studied wide-band gap II-VI semiconductors. Solar cells that use II-VI semiconductors and convert solar energy into electricity by the photovoltaic effect are near to being a source of practical renewable energy. A problem with these solar cells, however, is that they have a high cost of development. Therefore, many studies have investigated the use of CdTe, Cu-In-Ga-Se, and compound light absorption layers to replace silicon solar cells and yield the largest output at high efficiency. A particularly active area of this research is exploring thin film solar cells that use CdS/CdTe in the hetero-junction [1-3]. CdTe is a II-VI semiconductor with a direct band gap ($E_g = 1.44 \text{ eV}$ @ 300 K) that is easily processed and doped to become both n-type and p-type. CdTe is very useful in solar cells because it has a band gap that can show the best properties [1-5]. In addition, CdTe can be used as an X-ray and γ -ray detector because it has a larger atomic mass, a wider band gap than a-Se or other detector materials, and appropriate transmission performance. CdTe has been actively studied as a direct conversion X-ray detector because it has a higher atomic number and a fast electron-hole reaction speed, which gives it high X-ray sensitivity. Compared to

semiconductors with indirect detection like a-Se, the direct conversion-type detector has advantages such as digitized images, easy image storage and conversion, the video implementation, and high resolution [4, 5]. Using a CdS/CdTe hetero-junction, CdTe can be used as a thin film transistor (TFT) [6, 7]. However, the experimental performance of CdTe has not yet reached the theoretical maximum efficiency. In order to achieve this goal, it is necessary to study the surface morphology, deposition condition, and doping properties of CdTe.

The methods used for CdTe deposition include screen printing, evaporation, sputtering, close spaced sublimation, and chemical bath deposition [5-10]. In this study, we compared two types of 1- μm -thick thin films, one deposited by thermal evaporation and one deposited by radio frequency magnetron sputtering (RFMS), which were deposited at various substrate temperatures. Additionally, we also investigated the microstructures of CdTe thin films deposited by RFMS at RT that were post-annealed in air or vacuum at various temperatures.

Experimental

Generally, thin films have different microstructures and properties when prepared by different deposition methods. We therefore investigated the microstructures and properties of CdTe thin films prepared by RFMS or thermal evaporation. The CdTe thin films were deposited onto 50 mm $\times$ 50 mm non-alkali glass at various substrate temperatures (RT and 100, 200, 300, and 350 °C). Additionally, radio frequency (RF)-sputtered

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films prepared at RT were post-annealed in air or vacuum at various temperatures (200, 300, or 400 °C).

In thermal evaporation, the CdTe powder (99.99% purity) was evaporated using a Mo boat, and the distance between the source and substrate was 300 mm. The initial vacuum was set to 1×10^{-6} Torr, and it was maintained at 3×10^{-6} Torr during deposition. In addition, the T_s was RT or 100, 200, 300, or 350 °C.

In RFMS, a CdTe single target (50 : 50 at%, 99.99% purity) was used, and the base pressure and working pressure were 1×10^{-6} Torr and 7.5×10^{-3} Torr, respectively. The distance between the target and the substrate was 70 mm, and the RF power was maintained at 150 W. The CdTe thin films deposited without heating (at RT) were post-annealed in air or vacuum at 200, 300, or 400 °C for 1 hour.

To characterize the CdTe thin films, X-ray diffraction (XRD, Bruker gads), field emission scanning electron microscopy (FE-SEM, Hitachi), and tube furnace for annealing process (10-005, MUFFLE FURNACE) were used.

Results and Discussion

Generally, thin films deposited by evaporation had a larger grain size and higher crystallinity compared to the sputtered films due to low damage from adatoms during deposition. On the other hand, the thin films deposited by magnetron sputtering had poor crystallinity, small grain size, and sub-grains formed by secondary nucleation due to adatom bombardment. In this paper, we analyzed the microstructures of 1- μ m-thick CdTe thin films that were deposited by evaporation or RFMS at various substrate temperatures. XRD and FE-SEM were used to analyze and compare the microstructures of CdTe thin films deposited by the two different methods.

Fig. 1 shows the XRD patterns of CdTe thin film

deposited by thermal evaporation at various substrate temperatures. [(a) RT, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 350 °C, (f) FWHM of the C-(111) peak], where C-means cubic crystal structure. All films had a preferred orientation of C-(111) at $2\theta = 23.8^\circ$, which indicates they had a zinc-blende structure [JCPDS No.190193]. In addition to the preferential orientation C-(111), the growth of C-(220) at $2\theta = 38^\circ$ and of C-(311) at $2\theta = 46^\circ$ was observed when the T_s was increased to 350 °C, while the intensity and FWHM of the C-(111) peak decreased with increasing T_s , which is confirmed by other studies [10, 11].

The preferred growth orientation of the films was C-(111), but other planes grew together as a result of an increase in nucleation density caused by an increase in the T_s during deposition. As a result, the intensity of C-(111) decreased with an increase in random orientation that resulted from the growth of other planes. At the same time, however, the grain size increased due to the growth of activated nuclei, which was caused by a decrease in nucleation density that resulted from an increase in the adatom migration energy during deposition.

This phenomenon could be identified using the Harris analysis. This analysis compares the observed relative peak intensities in the X-ray patterns with those expected from a powder assumed to be entirely random to give the texture coefficient, i.e. the possibility that a given plane is parallel to the substrate. They also confirmed that preferred orientation changed from C-(111) to C-(220) and C-(311) with increasing T_s [11-13]. As shown in Fig. 1(f), the FWHM of the C(111) peak decreased with increasing T_s . According to the Scherrer equation,

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

where τ is the grain size, κ is the shape factor, β is the FWHM, λ is the wavelength, and θ is the Bragg angle.

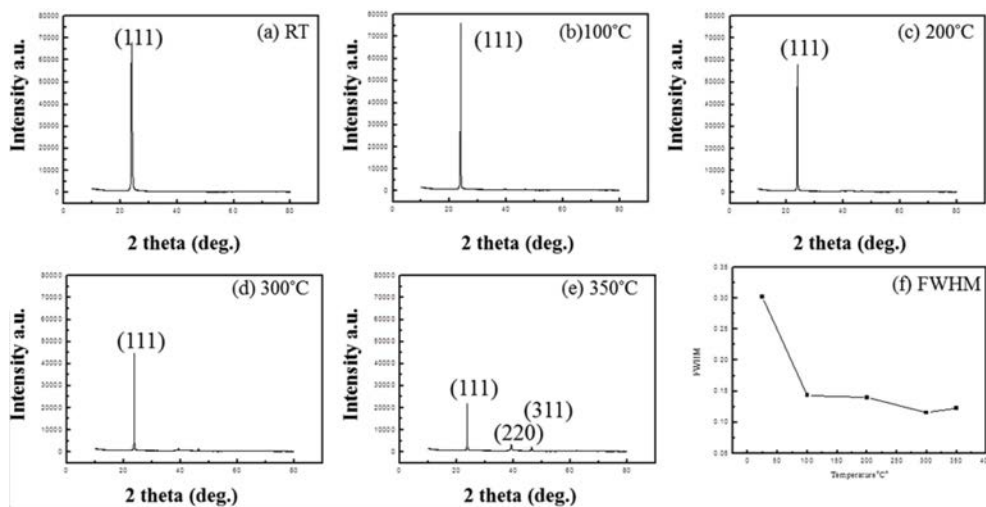


Fig. 1. XRD patterns and FWHM of CdTe films with thickness of 1 μ m films deposited by thermal evaporation at various substrate temperatures [(a) RT, (b) 100, (c) 200, (d) 300, (e) 350 °C, (f) FWHM of C-(111) peak].

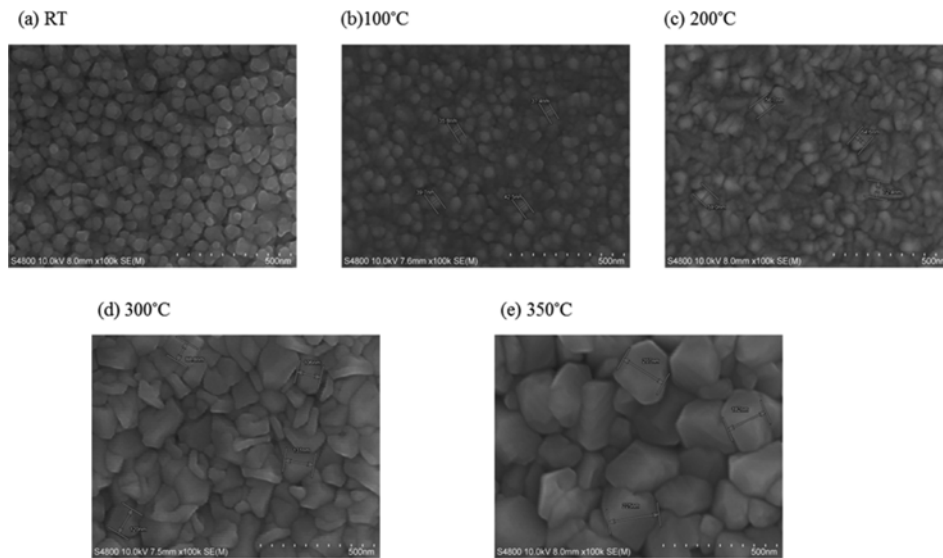


Fig. 2. SEM images of CdTe 1 μm films deposited by thermal evaporation at various substrate temperatures. [(a) RT, (b) 100, (c) 200, (d) 300, (e) 350 $^{\circ}\text{C}$].

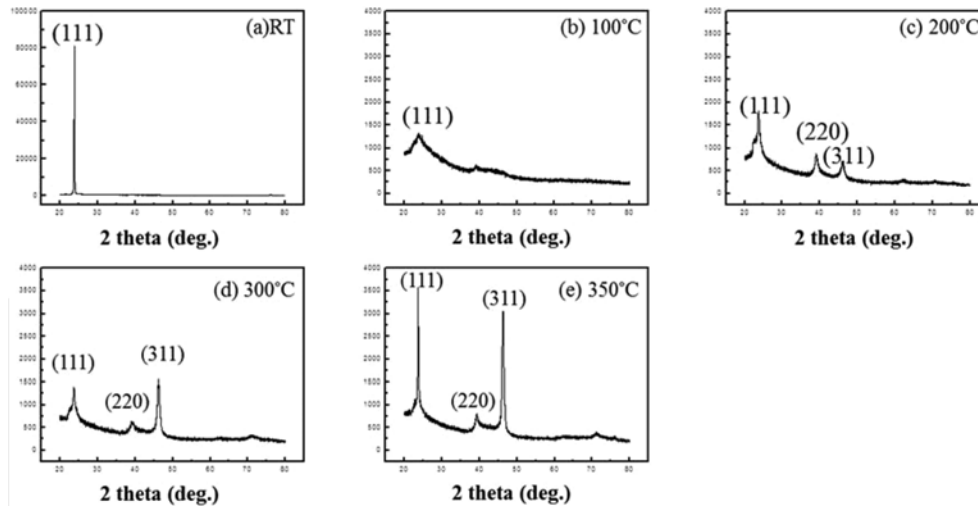


Fig. 3. XRD patterns of CdTe 1 μm films deposited by RFMS at various substrate temperatures [(a) RT, (b) 100, (c) 200, (d) 300, (e) 350 $^{\circ}\text{C}$].

When the FWHM is decreased, the grain size (τ) increases. This indicates that the growth of the CdTe film is affected by the T_s during deposition.

Fig. 2 shows surface FE-SEM images of the CdTe films prepared at different T_s . When the substrate was not heated, the grain size was approximately 50 nm [Fig. 2(a)]. When the substrate was heated to 350 $^{\circ}\text{C}$, the grain size increased to 150 nm, but the grain uniformity decreased. In other words, the grain uniformity decreased as result of the growth of small grains, not in the preferential C-(111) orientation, when the substrate was heated. This result is in agreement with earlier XRD/FWHM studies [4, 7], and indicates that when the T_s increases, other planes than the preferred C-(111) orientation are grown as a result of increased nucleation density. As a result of these higher deposition temperatures, the grain size is larger but the uniformity is decreased.

Fig. 3 presents the XRD patterns of CdTe films deposited by RFMS at various T_s . [(a) RT, (b) 100 $^{\circ}\text{C}$, (c) 200 $^{\circ}\text{C}$, (d) 300 $^{\circ}\text{C}$, (e) 350 $^{\circ}\text{C}$]. The RFMS method shows opposite to the thermal evaporation method. As shown in Fig. 4(a), the CdTe film deposited by RFMS without substrate heating has preferred orientation C-(111) at $2 = 23.8^{\circ}$, which is consistent with the growth in the evaporated film. However, when the T_s was increased, the results were different. The intensity of the C-(111) peak decreased sharply when the T_s was 100 $^{\circ}\text{C}$, and the film was amorphous. In evaporated films, the C-(111) peak is eliminated and the C-(220) and C-(311) peaks are increased. By contrast, in the sputtered films, the adatoms had higher energy, which made it easier for the C-(220) and C-(311) planes to grow.

Fig. 4 shows surface SEM images of the film grown by RFMS at various T_s . As illustrated in the XRD

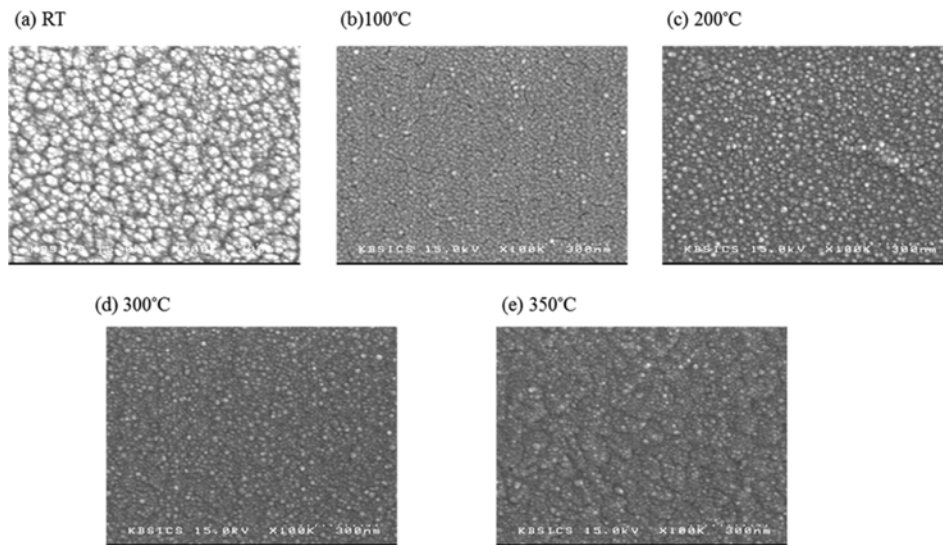


Fig. 4. SEM images of CdTe 1 μm films deposited by RFMS at various substrate temperature [(a) RT, (b) 100, (c) 200, (d) 300, (e) 350 $^{\circ}\text{C}$].

results, the grain size was largest when the substrate was not heated, and there was no significant difference with increasing T_s . It is expected that affected by sputtering damage of high energetic particles while in nucleation and early stage of grain growth [7, 14, 15]. When the T_s increased from 100 to 350 $^{\circ}\text{C}$, the intensities of both the preferred orientation C-(111) and the C-(220) and C-(311) orientations increased. This increased growth of each plane resulted from easier migration of the high-energy adatoms when the substrate was heated [14-16].

During the growth of the thin film, nucleation and grain growth occurred first, and density increased. Next, secondary nucleation, grain growth, and channeling of each grain occurred [7, 14]. In the case of films grown by RFMS, the atoms hitting the film surface have higher energy, so, compared to films grown by thermal evaporation, the density of nucleation is higher and secondary nucleation, not grain growth, results from high-energy adatoms. This promotes growth in random orientations, rather than in the preferred orientation. Consequently, the grain size of the RFMS-grown CdTe film was smaller than that of the evaporated film due to the low crystallinity. These results indicate that the microstructure of the film is dominated by the initial nucleation and grain growth during the deposition process.

Pandey et al. studied a CdTe film prepared by pulsed laser deposition, and reported that (111) (located at $2\theta = 23.8^{\circ}$) was the preferred orientation when the energy of the laser pulse was low [8]. However, when the energy of the laser pulse was increased, other planes were predominantly grown. This is consistent with the results in this study, where growth in random orientations that was not observed at RT was observed when the adatoms had higher energy during deposition. As the microstructure of the CdTe films can be varied by controlling nucleation and the grain growth rate, the

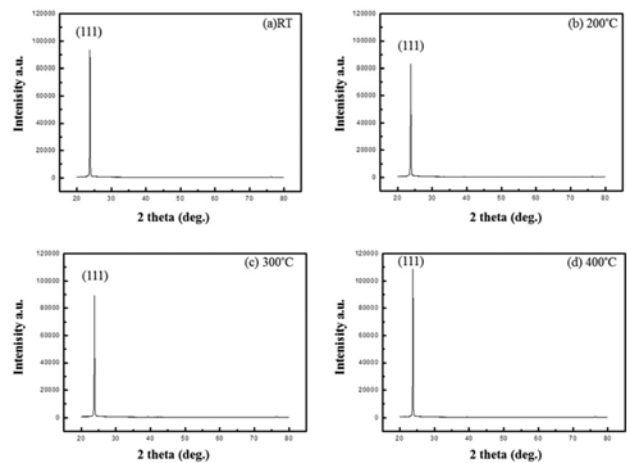


Fig. 5. XRD patterns of CdTe 1 μm films deposited by RFMS and post annealed in vacuum [(a) as-deposited, (b) 200, (c) 300, (d) 400 $^{\circ}\text{C}$].

properties of devices made from these films, such as photoconductors, can likewise be tailored.

Dzhafarov et al. reported that the XRD, peak for CdTe at $2\theta = 38^{\circ}$ corresponds to the hexagonal (110) orientation [6], while Enriquez *et al.* state that the preferred orientation is C-(220) [10]. To study the impact of post-deposition heating on the microstructure of the film, 1- μm -thick CdTe films were prepared by RFMS at room temperature and then post-annealed at various temperatures in vacuum or air. Fig. 5 and Fig. 7 show the XRD patterns of CdTe films deposited without substrate heating that were post-annealed at various temperatures in vacuum and air, respectively. Significant differences between these XRD patterns and those shown in Fig. 5 confirm the effect of the post-annealing step. When the substrate was heated during deposition, differences in the orientation of the deposited film were observed for different temperatures. However, in the case of post annealing, there was no

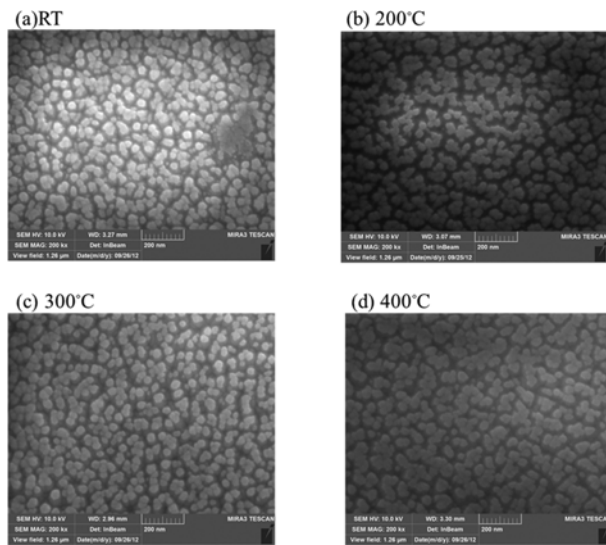


Fig. 6. SEM images of CdTe 1 μm films deposited by RFMS and post annealed in vacuum [(a) as-deposited, (b) 200, (c) 300, (d) 400 °C].

significant difference with annealing temperatures up to 400 °C. In addition, there was no difference in surface images and the intensity of the C-(111) peak.

Fig. 7 shows surface SEM images of sputtered films annealed at various temperatures in vacuum. These images show no difference in grain size and grain uniformity for different annealing temperatures. When the substrates were heated during deposition, atoms could easily diffuse in two dimensions on the film surface, and their diffusion was not hindered by grain barriers. However, atom diffusion during post-annealing occurred in three dimensions and encountered grain barriers, which meant that diffusion of atom required significantly more energy. Therefore, the film microstructure was impacted not only by the application of heat, but also by when that heat was applied. When the substrate was heated to 200 or 300 °C during deposition, differences in the microstructure of the film were evident. By contrast, when post-annealing heating up to 400 °C was applied to a film grown at RT, no changes in the film microstructure occurred. Bacaksiz *et al.* have reported that 400 °C is the critical temperature for changing the microstructure of CdTe films [7], but this value also depends on the film thickness and the deposition method. In this study, the thickness of film was 1 μm , while the film that Bacaksiz *et al.* used was 2 μm thick. Therefore, it is likely that if the annealing were performed at higher temperatures or for longer times, the film crystallinity might indeed be changed. Consequently, there are more changes in the post-annealing process than in substrate heating during deposition. This result indicates that the quality of devices containing CdTe thin films could be changed by using post-deposition thermal treatments above 400 °C to change the microstructure of the film [4].

The effect of annealing atmosphere was analyzed by

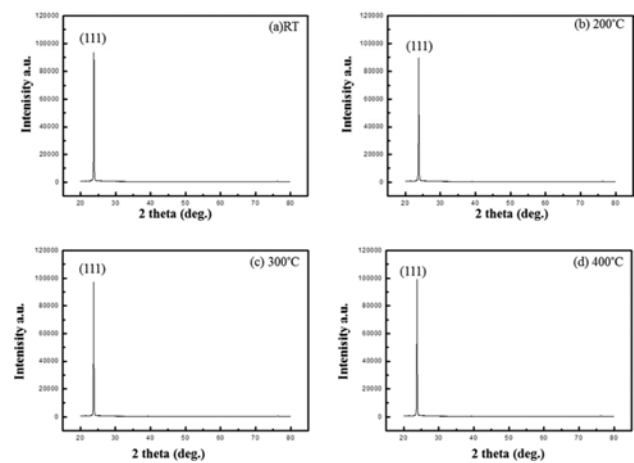


Fig. 7. XRD patterns of CdTe 1 μm films deposited by RFMS and post annealed in air [(a) as-deposited, (b) 200, (c) 300, (d) 400 °C].

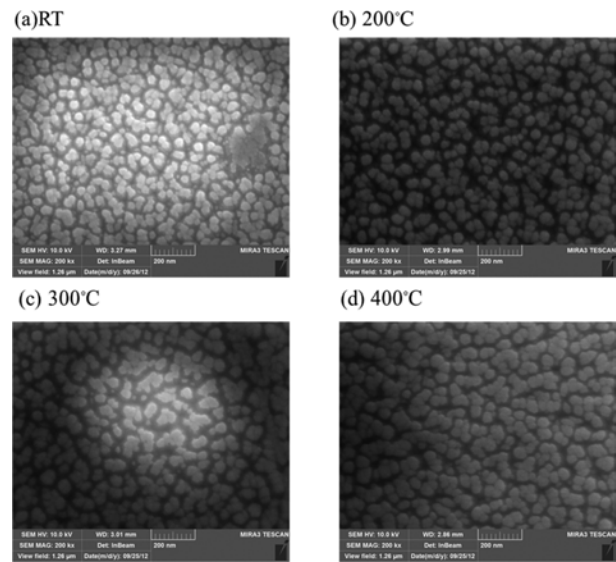


Fig. 8. SEM images of CdTe 1 μm films deposited by RFMS and post annealed in air [(a) as-deposited, (b) 200, (c) 300, (d) 400 °C].

comparing the films post-annealed in air and in vacuum. Overall, there was no significant difference in XRD patterns (Fig. 6 and Fig. 8) and surface grain size (Fig. 7 and Fig. 9). According to Enriquez *et al.*, [10] the XRD peak at $2\theta = 38^\circ$ is due to CdO, but Pandey *et al.* [8] claim it is due to CdTe hexagonal (110). There was no peak at $2\theta = 38^\circ$ in the film annealed in vacuum (Fig. 6), which indicates that the peak at $2\theta = 38^\circ$ is CdTe hexagonal (110). The CdO peak could be observed when changes were made to the film thickness, annealing time, or deposition temperature.

Conclusions

CdTe thin films with thickness of 1 μm were deposited by RFMS or thermal evaporation. Additionally, films prepared by RFMS at RT were annealed at various temperatures in air or vacuum. The evaporated films had larger grain size and higher crystallinity than the

sputtered films. The evaporated film had a preferred orientation of C-(111), but with substrate heating the XRD peak intensity of C-(111) decreased the intensities of the C-(220) and C-(311) peaks increased. This is likely due to the growth of other planes in random orientation as a result of substrate heating. According to the texture coefficient and standard deviation, the preferred orientation changed from C-(111) to C-(220) as a result of a change in the deposition temperature. Random orientation and the texture coefficient can also explain the fact that the sputtered films had lower crystallinity than the evaporated films. During sputtering, the adatoms had higher energy, and the bombardment of these adatoms caused the film to be amorphous when deposited at RT. When the substrate temperature was increased, film had preferred orientations of C-(220) and C-(311).

The CdTe films deposited by RFMS at RT were post-annealed at various temperatures in air or vacuum. The XRD patterns and surface images showed no differences with different annealing atmospheres. The results of the annealing experiment in air and vacuum confirmed that the peak observed near $2\theta = 38^\circ$ is CdTe hexagonal (110).

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