Properties of CdTe nanocrystalline thin films grown on different substrates by low temperature sputtering

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Abstract: CdTe nanocrystalline thin films have been prepared on glass, Si and Al_2O_3 substrates by radio-frequency magnetron sputtering at liquid nitrogen temperature. The crystal structure and morphology of the films were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM). The XRD examinations revealed that CdTe films on glass and Si had a better crystal quality and higher preferential orientation along the (111) plane than the Al_2O_3. FESEM observations revealed a continuous and dense morphology of CdTe films on glass and Si substrates. Optical properties of nanocrystalline CdTe films deposited on glass substrates for different deposited times were studied.

Key words: CdTe; thin films; RF magnetron sputtering; crystal structure; X-ray diffraction; optical properties

1. Introduction

In recent years, there has been growing interest in the synthesis of nanometer-sized II–VI binary semiconductor materials. Nanocrystalline semiconductor films are emerging as a new class of future photonic materials due to their unique nonlinear optical effects and quantum confinement[1, 2]. CdTe is an important II–VI semiconductor material, which is very useful for a variety of electro-optical devices and solar energy conversion[3−7]. Having a large exciton Bohr diameter (15.0 nm)[8], nanoscale CdTe probably possesses some unique physical properties with potential applications in optical devices, such as lasers and photodetectors. CdTe has a direct band gap in the range of 1.4–1.5 eV at room temperature, and its high absorption coefficient ($\sim 10^5$ cm^{-1}) makes it suitable for these purposes[9, 10]. Radio frequency (RF) magnetron sputtering is an effective technique to fabricate nanocrystalline films since it enables the control of size and volume distribution of nanoparticles over a wide range[11]. Further, substrates cooled at liquid nitrogen temperature are more favorable for the growth of nanocrystalline films[8]. During the film growth process, the temperature of the substrate is the key factor during the formation of the film structure since it may greatly affect the atom motilities and coalescences of the crystallites. Especially at low temperatures, it is possible to form small and continuous films on the substrates so that the adhering strength between the films and the substrates is improved[12]. Therefore, it is important to prepare nano thin films at low temperature. Figure 1 shows a schematic diagram of the RF magnetron sputtering system used in our experiments.

Although considerable progress has been made in the growth of CdTe nanocrystalline thin films[13, 14], the crystal quality, morphology, and optical absorption properties of CdTe nanocrystalline thin films deposited on various substrates have rarely been reported. In this work, we study the crystal quality of CdTe nanocrystalline films prepared on different substrates, such as glass, Si, and Al_2O_3. In addition, the influence of the deposition time on the structure and the quality of films will also be discussed.

2. Experimental details

The CdTe nanocrystalline thin films were deposited on three kinds of substrates (glass, Si, and Al_2O_3), which were cooled by liquid nitrogen. A CdTe target (99.999% purity) with a diameter of about 60 mm was used as the sputtering source. The substrate holder was a thick, stainless-steel plate (10 mm), which served as a cold finger (cooled by liquid nitrogen). The separation between the target and the substrates was about 60 mm. The flow rate of the sputtering gas Ar (99.99% purity) was set to 120 sccm and controlled by a mass flow controller, and the Ar pressure was fixed to 1.0 Pa. After the chamber was evacuated to a base pressure below 5.0 $\times 10^{-4}$ Pa, pre-sputtering of 10 min was carried out to clean the target surface. The RF power was 200 W with a frequency of 13.56 MHz. Then, the deposition of the films was carried
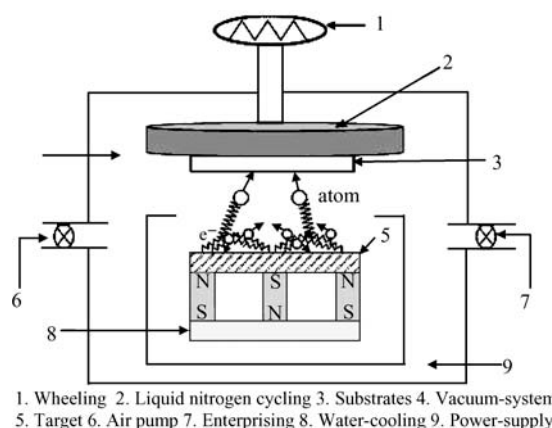

1. Wheeling 2. Liquid nitrogen cycling 3. Substrates 4. Vacuum-system
5. Target 6. Air pump 7. Enterprising 8. Water-cooling 9. Power-supply

Fig. 1. Schematic diagram of the magnetron sputtering system.
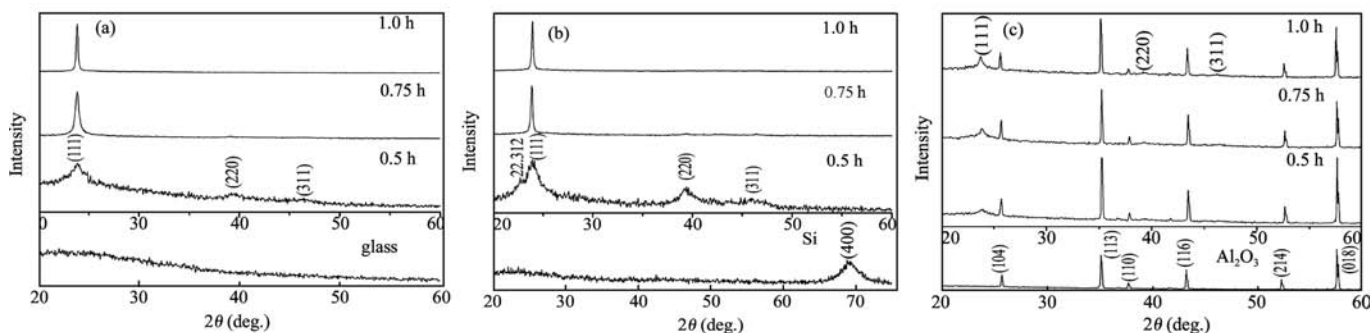
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Fig. 2. XRD patterns of CdTe films deposited on different substrates after different times: (a) Glass; (b) Si; (c) Al_2O_3.

Table 1. Calculated structural parameters of CdTe films deposited on different substrates.

Substrate	FWHM(111) (°)	Grain size (nm)	Deposition time (h)	Film thickness (nm)	Texture coefficient $TC_{111} = I(111) /[I(111) + I(220) + I(311)]$
Glass	0.481	17	0.5	479	0.557
	0.326	23	0.75	633	0.900
	0.306	26	1.0	786	0.949
Si	0.776	12	0.5	359	0.478
	0.318	25	0.75	684	0.883
	0.303	26	1.0	906	0.940
Al_2O_3	0.505	14	0.5	445	0.565
	0.499	15	0.75	701	0.586
	0.495	15	1.0	838	0.605

out for 0.5, 0.75, or 1.0 h on glass, Si, and Al_2O_3 substrates, respectively. The crystal structures of the products were examined by X-ray diffraction (XRD) using a Japan Mac science 18 kW X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm). Scanning electron microscopy (SEM) images of the films were obtained by a field-emission scanning electron microscope (FE-SEM, Philips XL-30). The optical spectroscopic measurements were carried out in the transmission and reflectance mode using a TU-1221 spectrophotometer.

3. Results and discussion

Figure 2 shows the XRD patterns of three sets of films on glass, Si, and Al_2O_3 with different sputtering times of 0.5, 0.75, and 1.0 h, respectively. All XRD patterns of the films could be indexed based on the cubic phase of CdTe (space group F-$\overline{4}$3m) with a lattice constant of a = 6.482 Å (ICDD 65-8395).

It was observed from Fig. 2(a) that three reflections of cubic CdTe could be identified in the XRD pattern of the film deposited on a glass substrate with a deposition time of 0.5 h, indicating the emergence of crystallization. The high background was due to the amorphous glass substrate. Films prepared for a longer time of 0.75 and 1.0 h possessed better crystallinity. Their XRD patterns exhibit higher preferential orientation at $2\theta \approx 23.922$° corresponding to the (111) reflection of the cubic CdTe. The fact that the XRD spectra of films deposited for longer time are dominated by the (111) reflection, is probably due to an increased diffusivity of atoms in the substrate, which allows the deposition on the (111) plane to occur

easily since the (111) plane has a lower surface energy than the (220) and (311) planes during the growth of nanocrystalline CdTe films[15, 16]. The XRD pattern of the films deposited on glass is consistent with the results in Ref. [10]. Moreover, we find that our films possessed a better crystallinity. Furthermore, the three reflection peaks had very wide profiles, implying a small grain size or imperfect crystallinity of the film. Using the full-width at half-maximum (FWHM) of the (111) diffraction peak of the XRD patterns, we calculated the grain sizes of the films by using the Debye–Scherrer formula $D = 0.9 \lambda / \beta \cos \theta_0$, where λ is the wavelength of the X-ray radiation, β is the FWHM of the peak and θ_0 is the Bragg angle[17]. The calculation results and some other data of films are given in Table 1.

Figure 2(b) shows the XRD patterns of CdTe films on Si substrates for different deposition times. A similar trend to Fig. 2(a) could be found in the patterns. It is worth to mention the occurrence of a satellite line (22.312°) on the left shoulder of the (111) reflection of cubic CdTe, as seen from Fig. 2(b). The unique diffraction line cannot be accounted for on the basis of the known CdTe single-phase structures, nor does it indicate the presence of Te crystals within the films. The observed satellite diffraction line is believed to be a characteristic signature of polytypism in the crystals.

Figure 2(c) shows the XRD patterns of CdTe films on Al_2O_3 for different deposition time. The diffraction peaks at $2\theta \approx 25.686$°, 35.264°, 43.487°, 52.664°, and 57.633° correspond to (104), (113), (115), (214), and (018) reflections of the Al_2O_3 structure (ICDD 46-1212), respectively. The diffraction peaks in the CdTe spectra exhibit a small in-
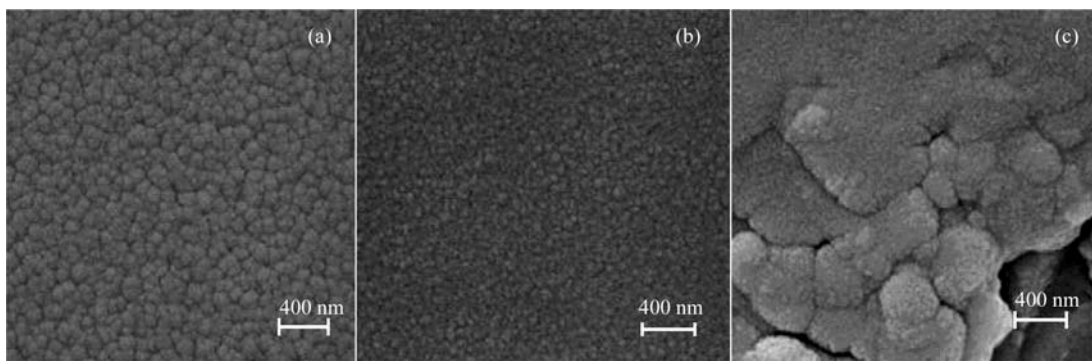
Fig. 3. SEM micrographs of CdTe films deposited on different substrate types: (a) Glass substrate, 1.0 h; (b) Si substrate, 1.0 h; (c) Al_2O_3 substrate, 1.0 h.
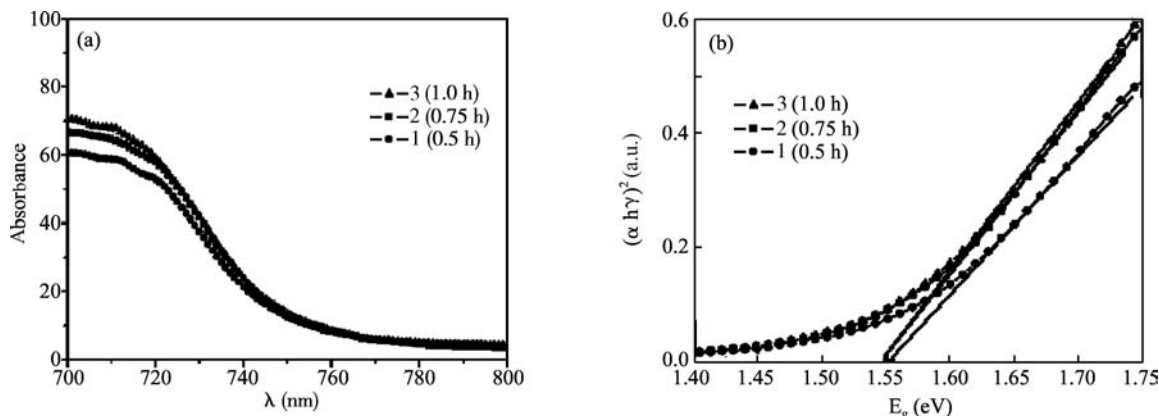

Fig. 4. (a) Absorption spectra of nanocrystalline CdTe thin films prepared on glass substrates for different deposition times: Curve 1 with 1.0 h; Curve 2 with 0.75 h; Curve 3 with 0.5 h. (b) Tauc spectra of nanocrystalline CdTe thin films prepared on glass substrates for different deposition times: Curve 1 with 1.0 h; Curve 2 with 0.75 h; Curve 3 with 0.5 h.

crease of diffracted intensity with increasing film thickness. To further evaluate the crystal quality of the films, the texture coefficient (TC_{hkl}), the thickness of the nanocrystalline CdTe films, and the grain sizes on different substrates are listed in Table 1. TC_{hkl} is a factor indicating the degree of (hkl) plane preferential orientation[18], which can be expressed as

$$TC_{hkl}(\%) = \frac{I_{hkl}}{\sum\limits_i I_{h_ik_il_i}} \times 100, \qquad (1)$$

where I_{hkl} is the diffraction intensity of plane (hkl), and $\sum_i I_{h_ik_il_i}$ is the sum of the intensity from all reflections. It is seen that the TC_{111} of the films increases with their thickness. For the CdTe/glass film, TC_{111} has a maximum value of 0.949. The value of 0.940 for CdTe/Si is smaller. The CdTe/Al_2O_3 film has the smallest value of 0.605 for a deposition time of about 1 h. This indicates that the CdTe/glass and CdTe/Si films have a higher preferential orientation along the (111) plane than the CdTe/Al_2O_3 film.

Figure 3 shows the SEM images of CdTe thin films grown on glass (Fig. 3(a)), Si (Fig. 3(b)), and Al_2O_3 (Fig. 3(c)). It can be seen that the films were composed of a large number of nanoparticles. The nanoparticals clustered together with a size of about 80 nm, and the boundary of the clusters is seen from Fig. 3(a). A similar phenomenon can be observed in Fig. 3(b) with a smaller cluster of about 35 nm. Figures 3(a) and 3(b) reveal a continuous and dense morphol-

ogy of the CdTe/glass and CdTe/Si films. However, it is also found that the nanoparticles adhered together and had some large holes, as observed from Fig. 3(c). The surface of the substrate is probably the factor that leads to a clustering of the nanoparticles, and the cluster images of the films on the Al_2O_3 substrates are not compared with other images found in the literature because they have rarely been reported. The SEM images of the films grown on glass are similar to the results of the CdS/glass films in Ref. [11].

The average grain size values measured by SEM are quite similar to those calculated from XRD peak widths. The average grain size is about 25 nm on glass and Si substrates. The SEM pictures show that the surface of the substrate has a great influence on the morphologies of the films. Smooth substrates, such as glass and Si, are better suited for the growth of nanocrystalline films than Al_2O_3.

The optical absorption behaviour of nanocrystalline CdTe films deposited on glass substrates depends on the size and concentration of the CdTe nanocrystallites. Figure 4(a) shows the absorption spectra of nanocrystalline CdTe films deposited on glass substrates for different deposition time (curve 1 with 0.5 h, curve 2 with 0.75 h, and curve with 1.0 h). The optical absorption coefficient of the films increases slightly with increasing deposition time (curve 1 to curve 3). This leads to a small shift of the absorption edge from 750 nm to longer wavelengths since the CdTe nanocrystals increase

slightly from 17 to 26 nm, as shown in Table 1. The absorption spectra of nanocrystalline CdTe thin films prepared on glass substrates show the same results as absorption spectra of CdTe/TiO$_2$[8].

The optical band gaps (E_g) of the CdTe films with different grain sizes are determined from ($\alpha h v$)^2 versus hv plots[19]. Figure 4(b) shows that E_g increased from 1.54 to 1.56 eV with a decrease of the grain diameter from 26 to 17 nm, corresponding to an increasing deposition time (curve 1 to curve 3). It should be noticed that the E_g values in our nanocrystalline CdTe films were higher than the band gap of bulk CdTe (1.45 eV). With the increase of the deposition time, the band gap increased slightly due to the decrease of the grain size. The blue-shift in the band-edge relative to the bulk CdTe values following a reduction in crystal size is attributed to the effect of quantum confinement on the electron band structure of CdTe[20].

4. Conclusion

CdTe films grown on glass and Si have better crystal quality and higher preferential orientation along the (111) plane than films grown on Al$_2$O$_3$. Moreover, we find that our films possessed a better crystallinity. The surface of the substrate has a great influence on the morphology of the films. Smooth substrates, such as glass and Si, are better for the growth of nanocrystalline films than Al$_2$O$_3$ substrates. The optical absorption behavior of CdTe thin films depends on the size and concentration of CdTe nanocrystallites. A blue-shift of the band-edge relative to bulk CdTe values is observed with the reduction in crystal size.

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