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Effects of deposition parameters on $Cd_{1-x}Zn_xTe$ films prepared by RF magnetron sputtering

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Abstract: $Cd_{1-x}Zn_xTe$ films were deposited by RF magnetron sputtering from $Cd_{0.96}Zn_{0.04}Te$ crystals target at different substrate temperatures, RF powers and working pressures. After deposition, the samples were annealed in high purity air at 473 K. The films were characterized using step profilometer, UV-VIS-NIR spectrophotometer, XRD and SEM. Depending on the deposition parameters and annealing, the values of the band gap of the CZT films varied between 1.45 and 2.02 eV.

Key words: $Cd_{1-x}Zn_xTe$; thin films; RF magnetron sputtering; band gap

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沉积参数对射频磁控溅射制备的碲锌镉薄膜的影响

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摘要:采用 $Cd_{0.96}Zn_{0.04}Te$ 靶,利用射频磁控溅射制备碲锌镉薄膜,通过改变基片温度、溅射功率和工作气压,制得不同的碲锌镉薄膜.将制备的碲锌镉薄膜放置在高纯空气气氛中,在 473 K 温度下退火.利用台阶仪、分光光度计、XRD 和 SEM 测试设备表征,结果表明,通过退火和改变沉积参数,可以制备出禁带宽度在 1.45 ~2.02 eV 之间调节的碲锌镉薄膜.

关 键 词:碲锌镉;薄膜;射频磁控溅射;带隙

中图分类号:O484.1　　**文献标识码**:A

Introduction

The $Cd_{1-x}Zn_xTe$ (CZT) is known as a direct wide-band gap semiconductor. Its band gap can be tailored between 1.45 eV (CdTe) and 2.26 eV (ZnTe) by adjusting the film composition. CZT is one of the important semiconductor materials used in the top cell of tandem solar cells, electro-optical modulators, photoconductors, light emitting diodes, X-ray and gamma ray detectors, etc.[1-4].

In recent years, research and applications of CZT alloy films grown by RF magnetron sputtering in thin-film solar cells have attracted more and more attention from some researchers. RF magnetron sputtering is one of the best options for commercialization, having the advantages of simple and low cost instrumentation, good reproducibility, high efficiency of material utilization and high growth rate.

In order to get CZT films with desirable properties, different RF magnetron sputtering technologies have been applied. CZT films were prepared using interdiffusion of sputtered layers of CdTe and ZnTe[5].

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CZT films were also tried by co-sputtering from a ZnTe-Cd target[6]. Multilayered CdTe/Zn structures were deposited by a multilayer method[7]. In this work, CZT films were grown by RF magnetron sputtering on glass substrates, using $Cd_{0.96}Zn_{0.04}Te$ crystal target with 50 mm diameter. The characteristics of the as-grown films have been investigated by step profilometer, UV-VIS-NIR spectrophotometer, XRD and SEM.

1 Experimental

CZT films were fabricated by RF magnetron sputtering on glass substrates. The sputtering target was cut from $Cd_{0.96}Zn_{0.04}Te$ ingot with diameter of 50 mm. The sputtering chamber was evacuated to a pressure less than 3.0×10^{-3} Pa. Argon (99.999%) was admitted under control (gas flow 28.7sccm) through a needle valve. The RF powers used in the growth process were 20 W, 36 W and 50 W at the working pressure 2.4 Pa. The working pressures used in the growth process were 2.0 Pa, 2.4 Pa and 3.8 Pa at the RF power of 36 W. A deposition time of 30 min was used. CZT films were deposited at different substrate temperatures: 473 K, 573 K and 673 K at working pressure of 2.4 Pa and RF power of 36 W. A deposition time of 60min was used in the growth process. A series of CZT films were prepared by changing the process parameters (see Table 1). CZT films deposited at different substrate temperatures were annealed in high purity air for 40 min at 473 K.

Table1 The preparation conditions of CZT thin films
表1 CZT薄膜的制备条件

	1#	2#	3#	4#	5#	6#	7#	8#
Power/W	20	36	36	36	50	36	36	36
Pressure/Pa	2.4	2.0	2.4	3.8	2.4	2.4	2.4	2.4
Substrate temperature/K	298	298	298	298	298	473	573	673
Sputtering time/min	30	30	30	30	30	60	60	60
Film thickness/nm	397	1 405	751	461	1 008	1 515	1 450	1 755

2 Results and discussion

Figures 1 ~ 3 show the transmission spectra for CZT films grown at various deposition parameters. Figure 4 shows the transmission spectra of heat-treated CZT samples deposited at various substrate temperatures. The spectra have consistent features, including coherent district, absorption edge and full absorption area. The difference of all samples lies in absorption edge position. According to semiconductor theory, absorption edge position corresponds to band gap.

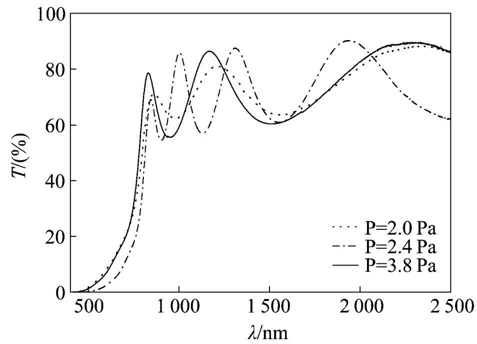

Fig. 1 Transmission spectra of CZT films deposited under different working pressures
图1 不同工作气压条件下制备的CZT薄膜的透射谱

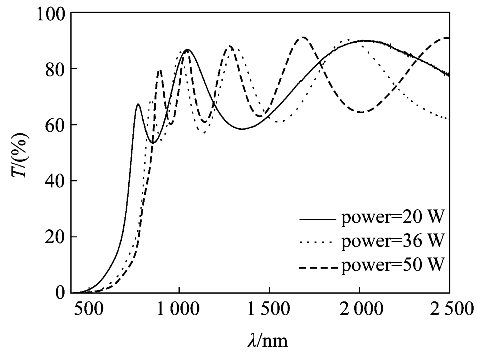

Fig. 2 Transmission spectra of CZT films deposited with different RF powers
图2 不同溅射功率条件下制备的CZT薄膜的透射谱

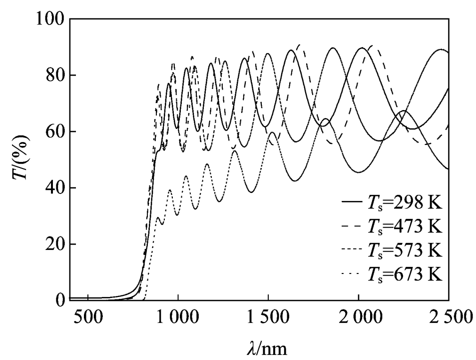

Fig. 3 Transmission spectra of CZT films deposited at different substrate temperatures
图3 不同基片温度条件下制备的CZT薄膜的透射谱

The transmission data are used to calculate absorption coefficient of the CZT films at different wave-

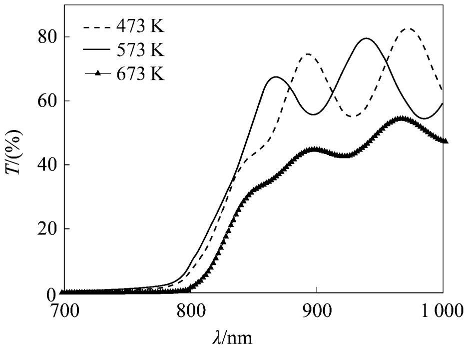

Fig. 4　Transmission spectra of heat-treated CZT films deposited at different substrate temperatures
图 4　不同基片温度下制备的 CZT 薄膜退火后的透射谱

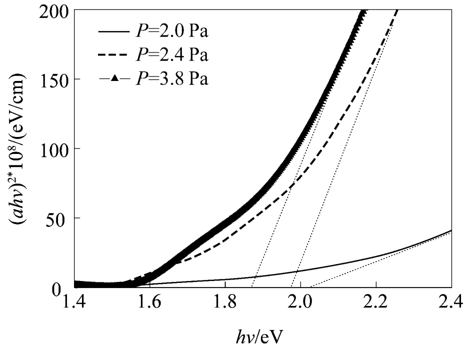

Fig. 5　$(\alpha h\nu)^2$ vs $h\nu$ plots of CZT thin films deposited under different working pressures
图 5　不同工作气压条件下制备的 CZT 薄膜带隙的拟合结果

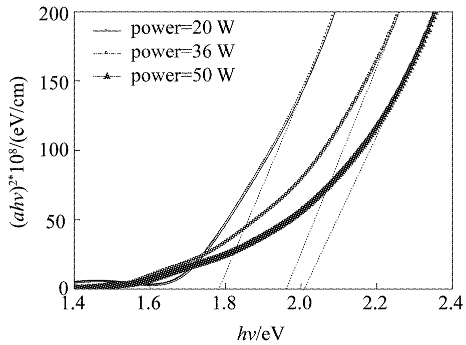

Fig. 6　$(\alpha h\nu)^2$ vs $h\nu$ plots of CZTthin films deposited with different RF powers
图 6　不同溅射功率条件下制备的 CZT 薄膜带隙的拟合结果

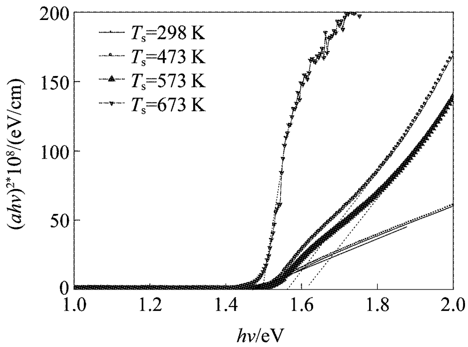

Fig. 7　$(\alpha h\nu)^2$ vs $h\nu$ plots of CZT thin films deposited at different substrate temperatures
图 7　不同基片温度条件下制备的 CZT 薄膜带隙的拟合结果

lengths. The absorption coefficient α is given by the relation[8]:

$$I = I_0 \exp(-\alpha d) \quad , \quad (1)$$

where I is the intensity of transmitted light, I_0 is the intensity of incident light and d is the thickness of CZT films.

As the transmittance is defined as I/I_0, we obtain from Eq. (1). In the high absorption region ($\alpha \geqslant 10^4$ cm^{-1}), the photon energy dependence of the absorption coefficient can be described by the quadratic relation[9]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad , \quad (2)$$

where ν is the frequency of the incident beam, A is a constant and E_g is the optical gap. So if we plot $(\alpha h\nu)^2$ vs $h\nu$ then the intercept of the straight line on the $h\nu$ axis gives us the value of band gap E_g. Plots of $(\alpha h\nu)^2$ vs $h\nu$ for CZT films are shown in Figs. 5 ~ 8, respectively. In order to determine the band gaps of all samples, plots in Figs. 5 ~ 8 were fitted. Table 2 is the fitting results of CZT thin films.

The direct band gap of the CZT film increases with the increase of RF power and decreases with the increase of working pressure.

Due to the difference of Ar plasma on the energy transfer efficiency of Cd, Zn and Te atoms, in the sputtering process, the quantitative relationship is[10]:

$$\gamma = \frac{4M_1M_2}{(M_1 + M_2)} \quad , \quad (3)$$

where M_1 is the quality of the incident ion (Ar^+), M_2 is the quality of the target atom. Energy transfer coefficient of Ar^+ on each atom can be computed accordingly: $\gamma_{Ar-Zn} = 0.94$, $\gamma_{Ar-Cd} = 0.78$, $\gamma_{Ar-Te} = 0.73$. So Zn atom shows sputtering advantage in the sputtered films. As RF power increases, the average energy of the sputtered particles is also enhanced . When the working

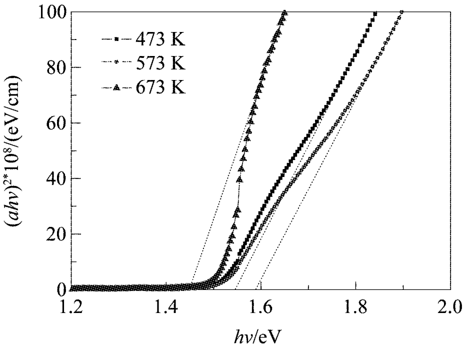

Fig. 8 $(\alpha h\nu)^2$ vs $h\nu$ plots of heat – treated CZT thin films deposited at different substrate temperatures
图 8 不同基片温度条件下制备的 CZT 薄膜退火后带隙的拟合结果

Table 2 The fitting results of CZT thin films
表 2 CZT 薄膜的拟合结果

	E_g/eV		ΔE_g/eV
		Annealed(473 K)	
1#	1.79		
2#	2.02		
3#	1.93		
4#	1.85		
5#	2.02		
6#	1.85	1.55	0.30
7#	1.65	1.59	0.06
8#	1.51	1.45	0.06

pressure is constant, the probability of collision of the sputtered particles with Ar^+ is unchanged. Therefore, the Zn content in the deposited films increases with increasing RF power. In addition, with increasing RF power, deposition rate increases, the thickness of the film in the same time is thickened.

In the vacuum chamber, the Ar^+ density becomes larger with increasing working pressure. It leads to increase probability of collision of the sputtered particles with Ar^+. The concentration fo Zn atom compared to Cd and Te atoms in the $Cd_{0.96}Zn_{0.04}Te$ target is very little. When RF power is certain, the final number of Zn atoms deposited on the substrate decreases with increasing working pressure. In addition, the deposition rate decreases with the working pressure increased, the thickness of the film in the same time becomes thinner.

In Fig. 9, the typical diffraction patterns for the as-deposited CZT films at different substrate temperatures are presented. It can be observed that the deposited films are polycrystalline with preferential (111) orientation. With increasing deposition temperature, the (111) peak becomes increasingly sharp. It indicates that crystalline quality of CZT film is improved with increasing substrate temperature.

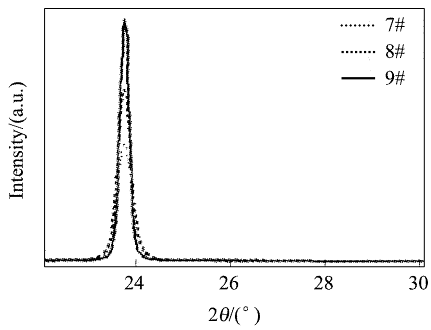

Fig. 9 XRD patterns of CZT films with different substrate temperatures
图 9 不同基片温度条件下制备的 CZT 薄膜的 XRD 图

Figure 10 shows SEM micrographs of CZT films grown at 473 K、573 K and 673 K. It shows that the non uniform spherical grains are distributed across the smooth glass substrate. The grain size progressively becomes bigger as the deposition temperature is increased.

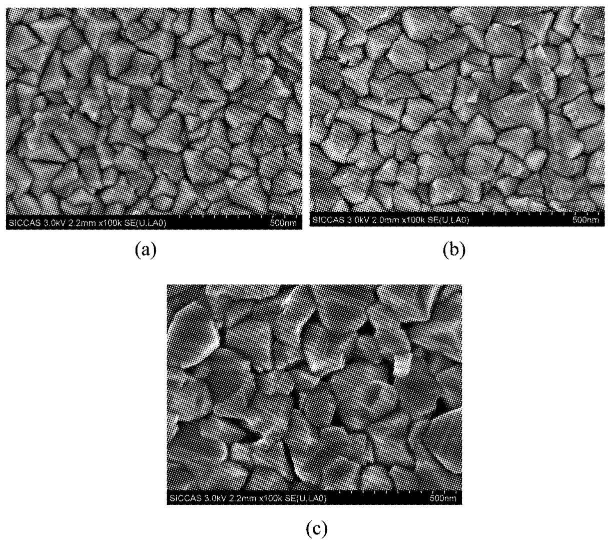

Fig. 10 SEM analysis of CZT thin films deposited in a vacuum 1 10-3Pa at different temperatures: (a) 498 K, (b) 573 K, (c) 673K
图 10 不同基片温度条件下制备的 CZT 薄膜的 SEM 图 (a)498 K, (b) 573 K, (c)673 K

The increased grain size may be resulted partly from kinetic factors during sputtering growth. The deposited films are polycrystalline with preferential (111) orientation, it indicates that the growth of CZT film at low temperature is kinetically limited. In the case of kinetically limited growth, it may be expected that grains with a faster growing orientation may grow at the expense of others[11]. This will result in a gradual increase in grain size. An additional factor is that recrystallisation and grain growth may take place dynamically during growth, especially at high growth temperature.

Because the sticking coefficient of Zn atom is less than Cd and Te atoms, when sputtering power and working pressure are constant, with the increasing of substrate temperature, adhesion of Zn atom on the substrate becomes poor. So the band gap of the CZT film decreases with the increase of substrate temperature[12].

It may be observed that the effect of heat treatment on the transmission spectrum of respective sample is different. The heat treatment determines the film transmittance, first increases (up to an substrate temperature of about 573 K) then decreases (Fig.4). The improvement of film crystallinity during heat treatment and the formation of the ZnO compound, transparent in the visible region, determine the increasing of transmittance for these samples. In the case of sample 8#, during heat treatment, the precipitation of the remaining tellurium excess induces a reduction of film transmittance, due to the strong optical absorption of tellurium in this wavelength range.

The obtained values of band gaps of CZT samples annealed are listed in Table 2. The heat treatment affects the band gaps of CZT films in a different manner, depending on the substrate temperatures. For CZT film deposited at 473 K, the value of band gap decreases from about 1.85 eV to 1.55 eV after heat treatment. In the case of CZT films deposited at higher substrate temperature, the variation of band gap as a consequence of the heat treatment is much lower. Annealing has greater impact on CZT films deposited at substrate temperature below the annealing temperature.

3 Conclusions

CZT thin films were obtained by RF magnetron sputtering on glass deposition from the $Cd_{0.96}Zn_{0.04}Te$ crystals target at different process parameters. The deposited films are polycrystalline with preferential (111) orientation. The band gap of the deposited films increases as RF power increases. The band gap of the deposited films decreases with increasing working pressure or deposition temperature. Heat treatment has an important influence on CZT films deposited at substrate temperature below the annealing temperature. By adjusting the heat treatment and preparation conditions, the band gap of respective CZT films can be tuned from 1.45 to 2.02 eV.

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