Effects of Sn-doping on morphology and optical properties of CdTe polycrystalline films*

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Abstract: Sn-doped CdTe polycrystalline films were successfully deposited on ITO glass substrates by close space sublimation. The effects of Sn-doping on the microstructure, surface morphology, and optical properties of polycrystalline films were studied using X-ray diffraction, scanning electron microscopy, and ultraviolet-visible spectrophotometry, respectively. The results show that the lower molar ratio of Sn and CdTe conduces to a strongly preferential orientation of (111) in films and a larger grain size, which indicates that the crystallinity of films can be improved by appropriate Sn-doping. As the molar ratio of Sn and CdTe increases, the preferential orientation of (111) in films becomes weaker, the grain size becomes smaller, and the crystal boundary becomes indistinct, which indicates that the crystallization growth of films is incomplete. However, as the Sn content increases, optical absorption becomes stronger in the visible region. In summary, a strongly preferential orientation of (111) in films and a larger grain size can be obtained by appropriate Sn-doping (molar ratio of Sn : CdTe = 0.06 : 1), while the film retains a relatively high optical absorption in the visible region. However, Sn-doping has no obvious influence on the energy gap of CdTe films.

Key words: CdTe polycrystalline films; Sn-doping; preferential orientation growth; morphology; optical properties; close space sublimation

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1. Introduction

As is well known, preferential orientation growth of films is a very complicated process and it often appears on crystal faces with a lower index of crystallographic plane. For example, preferential orientation growth of crystals with cubic phase often appears on (100), (110) and (111) crystal faces, etc. Also, preferential orientation depends on deposition conditions, especially substrate temperature[1]. Preferential orientation growth of crystals or films often greatly affects their properties, such as piezoelectric properties, thermoelectricity, elasticity and photovoltaic conversion efficiency[2–5]. In 1990, Saha *et al.* studied the effects of preferential orientation of CdTe crystalline films on photovoltaic properties. They found that photovoltage is related to the quantity of crystal faces with (220) and (311) preferential orientations under the same optical absorption conditions[6]. In 1998, Zhao *et al.* reported that polycrystalline silicon with alveolate preferential orientation has a high photovoltaic conversion efficiency of 19.8% and better resistant properties at high temperatures[5]. As a result of this find, polycrystalline silicon solar cells were developed further and more widely.

On the other hand, element doping is an efficacious method to improve the properties of materials. In 2003, Li *et al.* found that the conductivity of CdTe polycrystalline films could be dramatically improved by Te-doping[7]. As we all know, CdTe is the only material in the II–VI group compound semiconductors which can realize p-type doping and n-type doping. Doping of a certain element as a cation should have the equivalent effect on the photoelectric properties of CdTe despite films with different conductivities of p-type or n-type.

Due to the complexity of preferential orientation growth and the effectiveness of element doping, in this paper we fabricate Sn-doped CdTe polycrystalline films with preferential orientation growth of (111) using the close space sublimation method, and discuss the effects of Sn-doping on the morphology and optical properties of CdTe polycrystalline films.

2. Experiment

Lumpish pure (5N) polycrystalline CdTe was ground into a powder in an gate mortar. After being sieved, the CdTe powder and Sn powder were mixed together, and put into a ceramic boat as evaporator sources. The ceramic boat was put into a Ni heater which was fixed on the electrode in the vacuum chamber. ITO glass substrates with a size of 1.1 × 1.1 cm^2 were cleaned in abstergent, boiled in deionized water, and cleaned by sonic oscillation in an ethanol liquor. After being dried, they were put at 5 mm distance from the evaporator sources mentioned above. During the experiment, the evaporation temperature was controlled by adjusting the current through the Ni heater. When the vacuum of the deposition chamber

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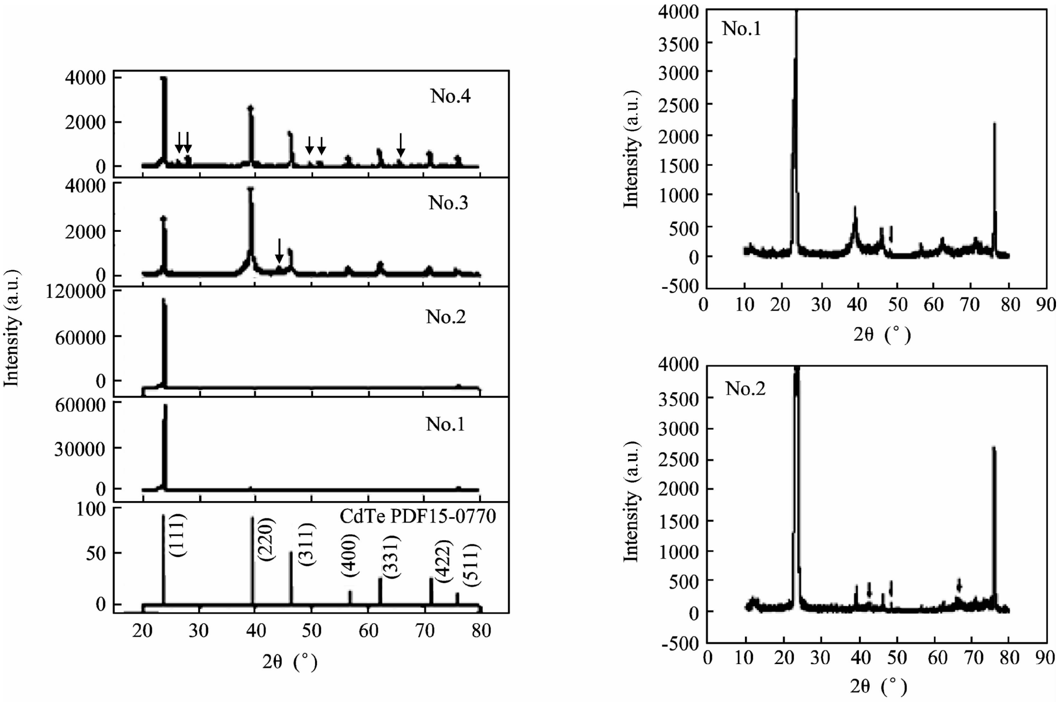

(a) (b)

Fig. 1. (a) XRD patterns of samples No. 1–No. 4; (b) Amplified pictures of No. 1–No. 2.

approached 10^{-3} Pa, the switch of the evaporator sources was opened to make the current flow across the Ni heater. The current increased up to 65 A with a speed of 2 A/min, and held for a deposition time of 15 min at 65 A. The samples prepared from molar ratios of Sn powder and CdTe powder of 0.03 : 1, 0.06 : 1, 0.125 : 1, 0.25 : 1 were designated as No.1–No.4, respectively.

The effects of Sn-doping on the microstructure, surface morphology, and optical properties of CdTe polycrystalline films were characterized using a MACSCIENCE 18 KW rotating target X-ray diffractometer from Japan (XRD, CuKα, 40 kV, 120 mA, continuous scanning), scanning electron microscopy (SEM, Leo1430VP, Germany), and an ultraviolet-visible spectrophotometer (UV-Vis, Tu-1221, China), respectively.

3. Results and discussion

3.1. XRD discussion

Figures 1(a) and 1(b) show the X-ray diffraction patterns of CdTe films with different Sn-doping contents. As seen in Fig. 1, all of the samples are CdTe with cubic phase blende structures [PDF 15-0770(ICDD, 2003)]. When the molar ratio of Sn to CdTe is lower (samples No.1 and No.2), the intensity of the (111) diffraction peak is very strong, which confirms that the films have complete preferential orientation of (111). As the molar ratio of Sn to CdTe increases (samples No. 3 and No. 4), the intensity of the (111) diffraction peak becomes clearly lower, which indicates incomplete crystallinity in the films. The full width at half maxima (FWHM) of the (111) diffraction peak in samples No.1–No.4 are 0.078°, 0.042°, 0.199°, and 0.121°, respectively. As we know, during X-ray diffraction analysis, FWHM is directly related to the grain size of the sample under the same measuring conditions. A larger FWHM indicates that the grain size becomes smaller along the direction of corresponding diffraction face. Thus, according to FWHM, the grain sizes of the four samples were deduced as No. 2, No. 1, No. 3, No. 4 by size in sequence. The crystallinity of films with larger crystal grains can be improved by appropriate Sn-doping (the molar ratio of Sn to CdTe is 0.06 : 1). Sign ↓ in Fig. 1 corresponds to the diffraction peaks of SnTe [PDF 39-0925(ICDD, 2003)]. As the radius of the Sn atom is larger than that of the Cd atom, Cd replaced by Sn would lead to the expansion of CdTe lattices. Moreover, the presence of SnTe made all the reflection peaks of the samples shift to the lower angular side. As unexpected, sample No. 3 has a preferential orientation of the (220) crystal face. This indicates that its surface morphology is different from the others.

3.2. Surface morphology discussion

Figure 2 shows the surface morphologies of samples No. 1–No. 4. The morphologies of samples are clearly different from each other. Sample No. 2 consists of a mass of polyhedral grains with diameters about 4 μm. These grains have obvious crystal faces, and grain boundaries are distinctly visible. Two typical grains with three crystal faces are indicated in Fig. 2(b). These three crystal faces are vertical to each other, and their confluence point is plumb or half-plumb the surface of the film. Allowing for the cubic structure of CdTe, the crystal face in these two typical grains parallel to the surface of the film can be concluded to be the (111) crystal face. In Fig. 2(b), most grains have the same characters as the two typical grains,

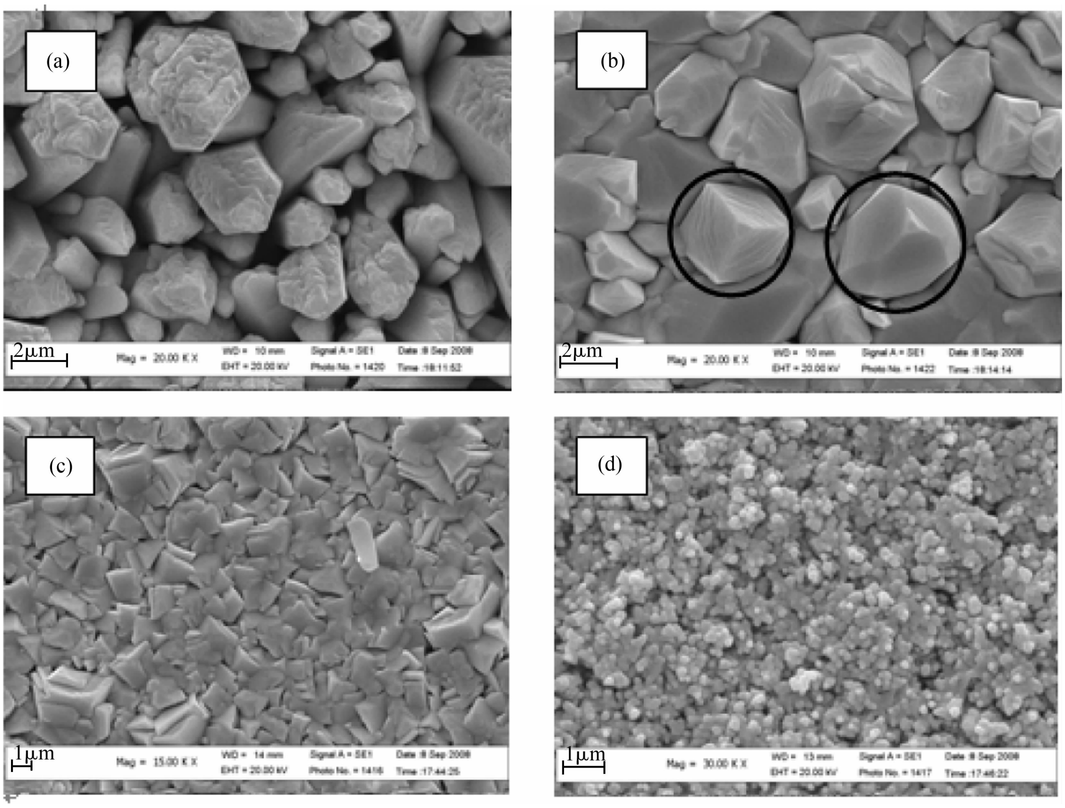

Fig. 2. SEM micrographs of samples No.1–No.4.

which dovetails with the conclusion in the XRD analysis that sample No. 2 has a strong preferential orientation of (111). In 2007, Major *et al.* attentively researched earlier morphologies of CdTe crystalline films prepared by close space sublimation using SEM. They came to the conclusion that the earlier growth process of crystalline CdTe films consists of an island growth process and an island combination process, which is called the two-step growth mechanism[8]. The growth mechanism of sample No. 2 accords with the two-step growth mechanism completely from its surface morphology. However, as the molar ratio of Sn to CdTe increases, the grains of polycrystalline films become smaller, and crystal boundaries become indistinct (Figs. 2(c), 2(d)), which made it impossible to distinguish the crystal faces of grains. These morphologies reveal that the island combination process was suppressed in the growth process of films and caused their growth mechanism to not accord with the two-step growth mechanism. In other words, during the growth process of CdTe polycrystalline film, the island combination growth process could not be completed because of the obstructive effect of Sn-doping.

3.3. Optical properties of samples

When the wavelength of incident light satisfies $\lambda < hc/E_g$, an electron in the valence band will absorb a photon from the incident light and transit from the valence band to the conduction band, which will conduce to a rapid rise in optical absorption. Figure 3 shows the optical absorption of samples No.1–No.4 measured at room temperature. Compared to bulk CdTe materials, all of their absorption bands have red shifts. As the molar ratio of Sn to CdTe increases, the optical absorption of the samples becomes stronger in the visible region. Figure 3 confirms that CdTe is a good absorption material, and absorption in the visible region can be improved by Sn-doping.

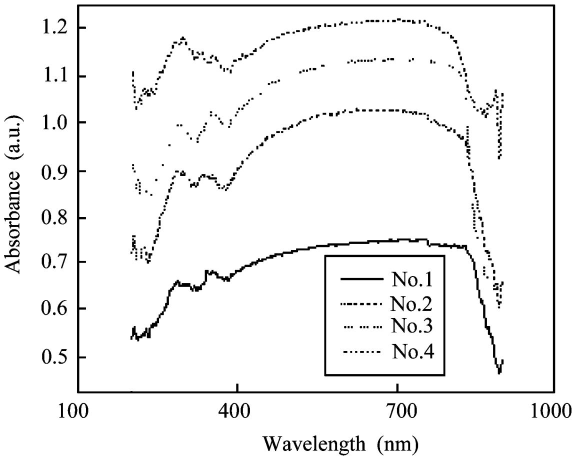

Fig. 3. Absorption spectra of samples No.1–No.4.

Using the Tauc formula[9], the dependence of $(\alpha h\nu)^2$ on $h\nu$ for the samples is plotted in Fig. 4, where α is the absorption coefficient and $h\nu$ is the energy of the incident photon. According to the energy gap formula: $\alpha h\nu = \text{const} \times (h\nu - E_g)^{1/2}$, the band gap E_g = 1.50–1.55 eV can be qualitatively determined by extrapolating the spectral curves to the energy axis (the straight line in the spectra). Compared with the standard value of 1.60 eV, the energy gap just has a small variation. This means that the change of Sn content in the samples has no obvious effect on the energy gap of CdTe polycrystalline films.

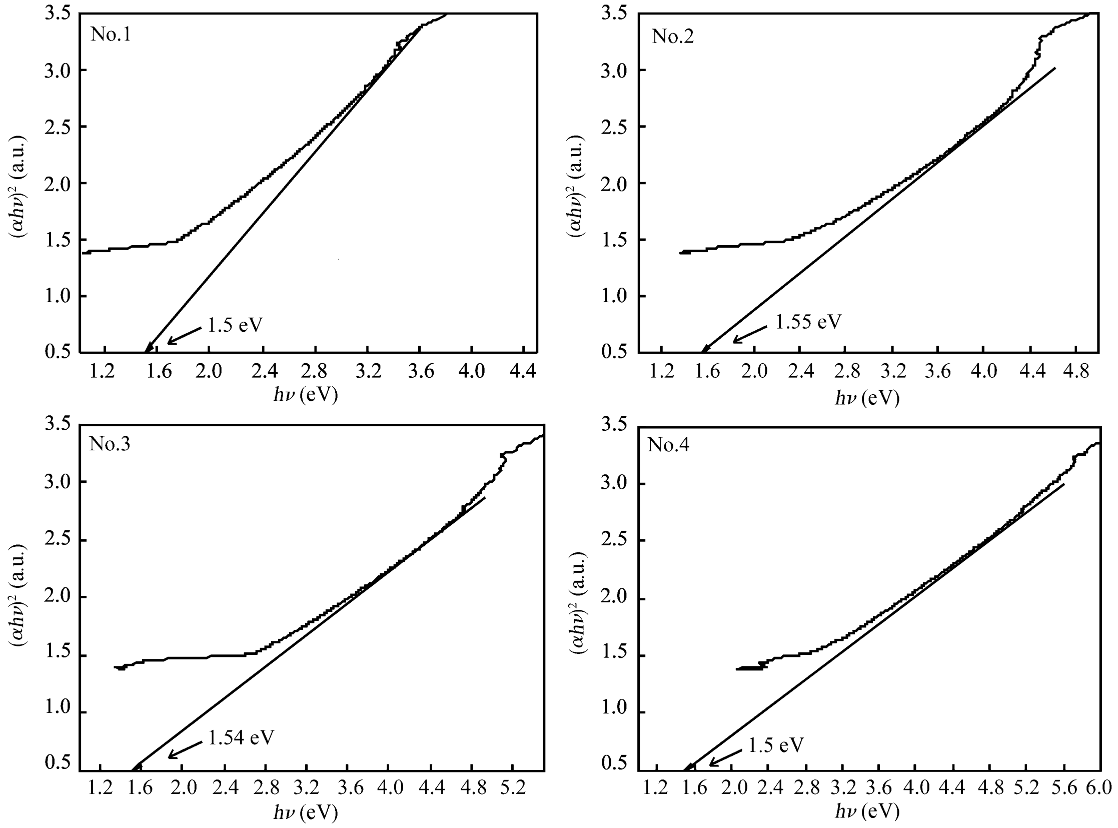

Fig. 4. Relation between $(\alpha h\nu)^2$ and $h\nu$ of samples No. 1–No. 4.

4. Conclusions

Sn-doped CdTe polycrystalline films were successfully prepared by close space sublimation. At smaller molar ratios of Sn and CdTe, the films composed of a mass of crystal grains with larger grain sizes had a strongly preferential orientation of (111). The growth process of films is in complete accord with the two-step growth mechanism. As the molar ratio of Sn and CdTe increases, preferential orientation of (111) in films becomes weaker, grain size becomes smaller, and the crystal boundary becomes indistinct, indicating that superfluous Sn-doping will suppress crystallization growth and cause incomplete crystallinity in CdTe films. However, as Sn content increases, optical absorption becomes stronger in the visible region, while a change of Sn-doping content has no obvious influence on the energy gap of CdTe films. In summary, it is concluded that strongly preferential orientation of (111) in films and larger grain sizes can be obtained by appropriate Sn-doping (molar ratio of Sn : CdTe = 0.06 : 1), while the film retains a relatively high optical absorption in the visible region.

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