

Research Article

Preparation and Characterization of Sb_2Te_3 Thin Films by Coevaporation

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Deposition of Sb_2Te_3 thin films on soda-lime glass substrates by coevaporation of Sb and Te is described in this paper. Sb_2Te_3 thin films were characterized by x-ray diffraction (XRD), x-ray fluorescence (XRF), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), electrical conductivity measurements, and Hall measurements. The abnormal electrical transport behavior occurred from *in situ* electrical conductivity measurements. The results indicate that as-grown Sb_2Te_3 thin films are amorphous and undergo an amorphous-crystalline transition after annealing, and the posttreatment can effectively promote the formation of Sb-Te bond and prevent oxidation of thin film surface.

1. Introduction

It is well known that CdTe thin film solar cell offers one of the most promising photovoltaic devices for terrestrial applications due to the near-optimum bandgap and high absorption coefficient of CdTe. However, forming an ohmic contact to CdTe is very difficult because of the high electron affinity of CdTe and the self-compensation in CdTe. An approach to overcoming these problems is incorporation of p^+ region materials between CdTe and the metal electrode to provide the advantageous electrical properties. These materials should have long-term stability of the electrical contact to CdTe and should not cause chemical reactions at the interface. Conventionally, a Cu layer or a material doped with Cu is used to form back contacts with a low barrier height. Unfortunately, Cu will diffuse along the grain boundaries down to the main junction resulting in the degradation of device performance. New material such as antimony telluride possesses the expected characteristics mentioned above, which can provide stable ohmic back contacts to CdTe [1, 2].

Antimony telluride is a binary V–VI group compound semiconductor with the form of A_2B_3 , which is mentioned as the thermoelectric generators and coolers, and back contacts

for photovoltaic devices because of its high Seebeck coefficient, low thermal conductivity, low electrical resistivity, low bandgap, and long-term stability [1–3].

To obtain Sb_2Te_3 thin films, a number of techniques have been used in the literature, such as thermal evaporation [4, 5], atomic layer epitaxy (ALE) [6], sputtering [2, 7], electrochemical method [8], flash evaporation [9], and metalorganic chemical vapor deposition (MOCVD) [10]. Among all these techniques, coevaporation offers several advantages in the growth of Sb_2Te_3 thin films for CdTe solar cells, such as the desirable stoichiometry, simple evaporation equipment, and a relatively short fabrication processing time.

In this study, we describe the preparation, structure, morphology, and electrical properties of coevaporated Sb_2Te_3 thin films. These are helpful to fabricate stable CdTe solar cells with Sb_2Te_3 back contacts.

2. Experimental

Sb_2Te_3 thin films were grown by a coevaporation method at room temperature in a high-vacuum chamber with base pressure about 9×10^{-4} Pa. Sb foil (99.999% purity) and Te powder (99.999% purity) were evaporated on the glass substrates from two independent sources. The deposition

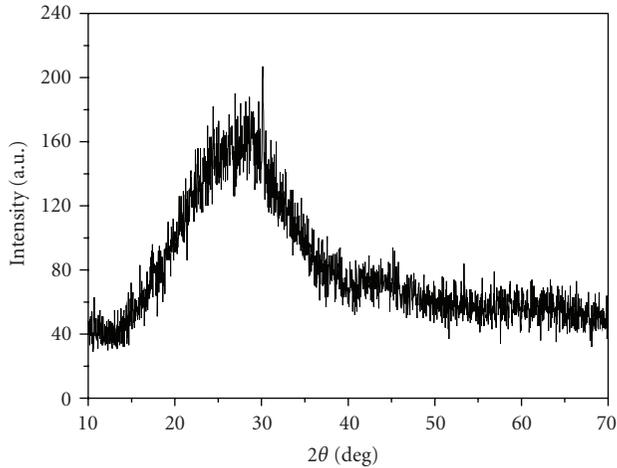


FIGURE 1: XRD pattern of Sb_2Te_3 thin films as-deposited.

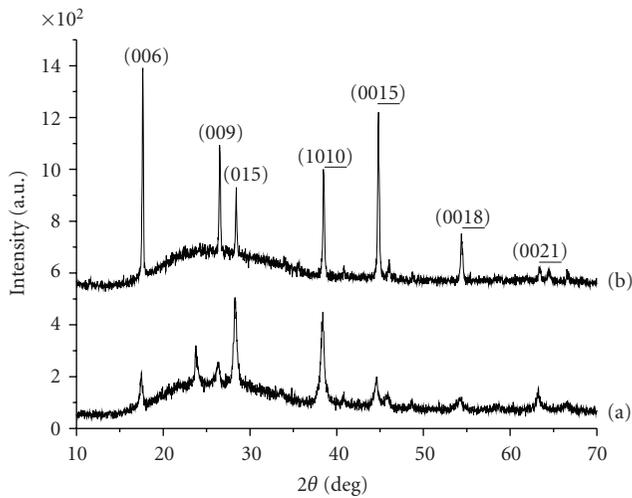


FIGURE 2: XRD patterns of Sb_2Te_3 thin films annealed at 473 K (a) and 613 K (b).

rates and the thickness of thin films were independently controlled by two LHC-2 thickness monitors. The substrates were cleaned prior to deposition, and a postdeposition treatment was performed in N_2 ambient.

XRD measurements were used to study the Sb_2Te_3 structure, and XRF was performed to determine chemical composition of the thin films. Surface analysis of Sb_2Te_3 thin films was carried out using XPS, and surface morphology of Sb_2Te_3 thin films was observed by AFM. Dark conductivity was measured with electron beam evaporation deposited Ni-strips using two-probe technology. The four-probe Van der Pauw method was used to carry out the Hall measurements to determine the Hall coefficient, mobility, and carrier concentration.

3. Results and Discussion

To determine the composition of the Sb-Te alloys, x-ray fluorescence spectra analysis of Sb-Te systems as-deposited

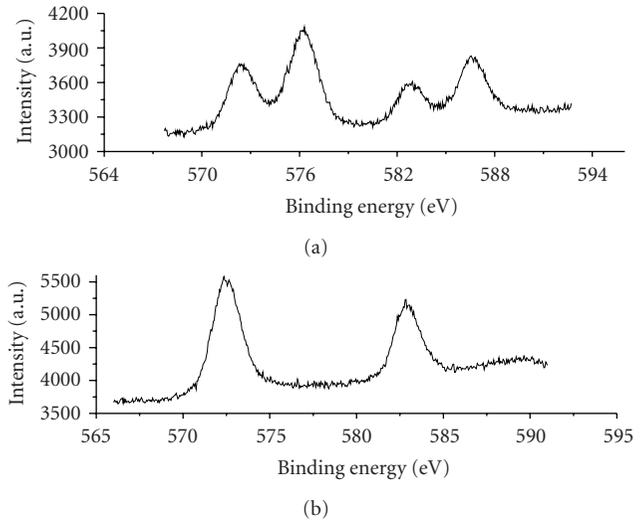


FIGURE 3: Te 3d spectra for Sb_2Te_3 thin films as-deposited (a) and annealed at 613 K (b).

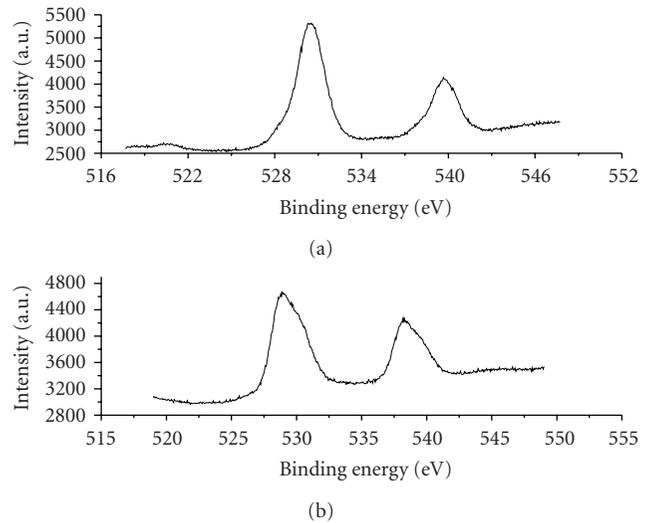


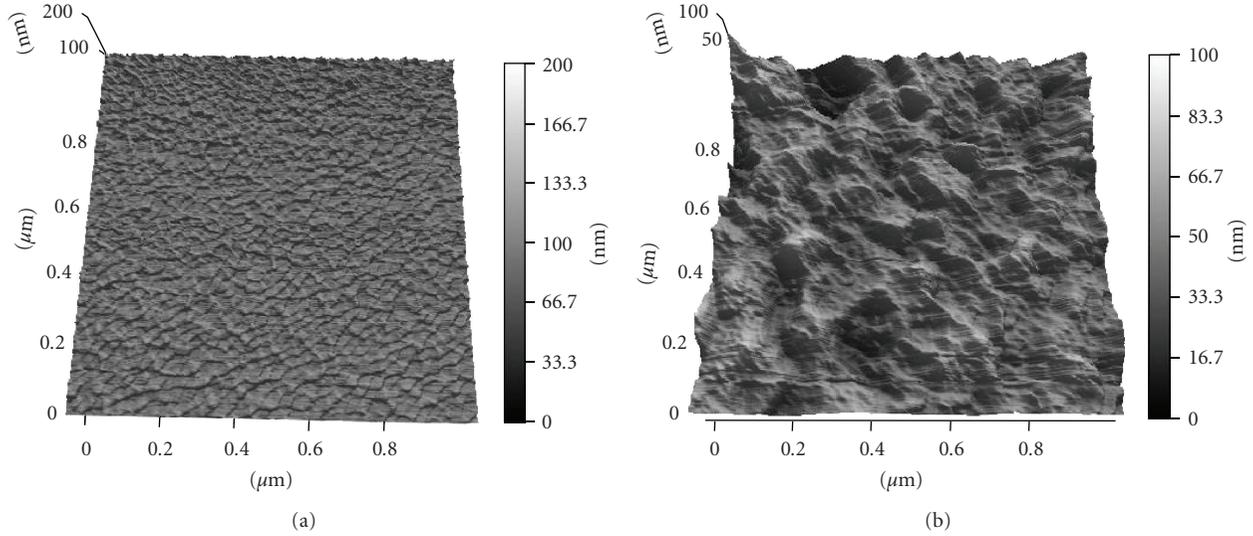
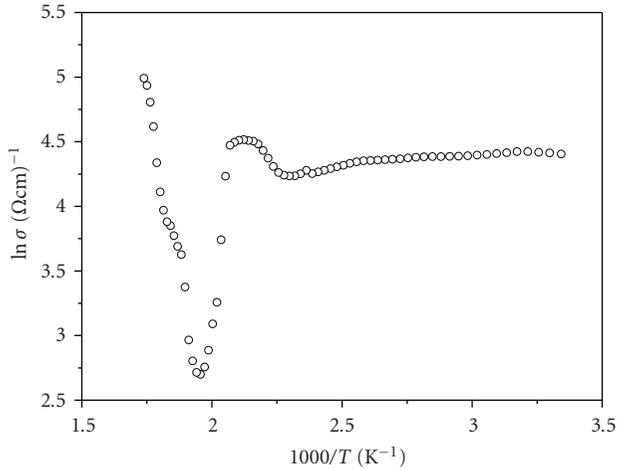
FIGURE 4: Sb 3d spectra for Sb_2Te_3 thin films as-deposited (a) and annealed at 613 K (b).

was carried out. The contents of two kinds of elements, Sb and Te, for as-grown thin films from XRF quantitative analysis are 0.0554 and 0.0941 mg/cm^2 , respectively. The stoichiometric ratio (Te:Sb) is 1.62:1 in the Sb_2Te_3 thin films, which is good agreement with the standard value, 1.5:1 (a relative error of 10% is assumed). After annealing, there are not significant changes of stoichiometry in the Sb_2Te_3 thin films.

Figure 1 shows x-ray diffraction pattern of Sb_2Te_3 thin films deposited by coevaporation at room temperature on the glass substrates. As-deposited Sb_2Te_3 films are an amorphous structure. Bätzner et al. [1], and Romeo et al. [2] have reported that Sb_2Te_3 thin films as the back contact materials were deposited on a substrate kept at a temperature of 573 K and, thus, CdTe solar cells with crystalline Sb_2Te_3

TABLE 1: Hall parameters for Sb_2Te_3 thin films.

Sample	Mobility ($\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$)	Hall coefficient ($\text{cm}^3 \text{C}^{-1}$)	Carrier concentration (cm^{-3})
Sb_2Te_3 as-deposited	44.49	0.082	7.60×10^{19}
Sb_2Te_3 annealed at 613 K	169.86	0.11	5.87×10^{19}

FIGURE 5: AFM images of Sb_2Te_3 thin films as-deposited (a) and annealed at 613 K (b).FIGURE 6: Temperature dependence of dark conductivity for Sb_2Te_3 films.

thin films demonstrated the good device performance. In this work, however, the films were deposited at room temperature, so the postdeposition treatment was desirable for Sb_2Te_3 ohmic contact to CdTe. It was found that it had no effect on the Sb_2Te_3 amorphous phase after annealing at a low temperature (<473 K). Then these samples were annealed at a temperature of 473 K in N_2 ambient, whose XRD pattern shown in Figure 2(a) reveals their polycrystalline nature with the peaks corresponding to (006), (009), (015), (1010), (0015), (0018), and (0021) planes of Sb_2Te_3 . Besides the

diffraction peaks of rhombohedra Sb_2Te_3 , the pattern shows a weak diffraction peak is present at about 2θ of 23.76° , which could be assigned to the TeO_2 due to the oxidation of thin film surface as confirmed by XPS analysis. The thin films were annealed at 613 K shown in Figure 2(b). The strongest intense line indicates the (006) plane is at about 2θ of 17.45° , and the additional weak peaks are at about 2θ of 17.5° , 26.4° , 28.4° , 40.8° , 44.8° , 54.5° , and 64.2° corresponding to the (009), (015), (1010), (0015), (0018), and (0021) planes of Sb_2Te_3 , while the weak diffraction peak of TeO_2 disappears at about 2θ of 23.76° . From Figure 2, one can see that an effect of the annealing temperature on the structure of the thin films, annealing at a higher temperature, would readily promote the formation of single-phase Sb_2Te_3 with very strong (001) preferential orientation and effectively suppress a TeO_2 secondary phase.

Figures 3–4 show the XPS spectra of Sb_2Te_3 thin films. Te 3d5/2 (572.5 eV) and Te 3d3/2 (582.9 eV) peaks are observed (Figure 3), which well agrees with the results reported for Sb_2Te_3 in the literature [11]. Additional peaks (576.2 and 586.6 eV) for Te 3d shown in Figure 3(a), indicating a chemical environment different from Sb_2Te_3 , can be ascribed to Te-O. The Te-O bond does not exist on the film surface after crystallization at 613 K, which indicates that as-deposited thin film surface is much easy to be oxidized after exposure to the atmosphere. For the Sb 3d spectra as shown in Figure 4, the values of 539.6 eV (3d3/2) and 530.3 eV (3d5/2) are ascribed to Sb-O bonding, and 529–530 eV (3d5/2) and 538–539 eV (3d3/2) to Sb metallic bonding [11, 12]. The Sb 3d peaks at 530.5 and 539.7 eV in Figure 4(a) correspond to Sb-O, which shows that as-deposited film surface easily

forms antimony oxide. Sb-Te bonds are demonstrated in polycrystalline films (Figure 4(b)) at 528.9 and 538.2 eV. Therefore, a postdeposition treatment is an effective method to promote the formation of Sb-Te bond and prevent oxidation of thin film surface.

The particle size and morphology of the Sb_2Te_3 as a back contact material affect the electrical properties of solar cells. Therefore, it is possible to evaluate the quality of the films by AFM. Figure 5 shows AFM images of Sb_2Te_3 thin films as-deposited (a) and annealed at 613 K (b). The films annealed at a high temperature exhibit larger particles than that as-deposited films, and the root mean square (RMS) values are about 2.3 nm for as-deposited films and 7.6 nm for the annealed films. Obviously, the posttreatment process can promote the growth of the films, which is significant to reduce the grain boundary density.

As a good buffer layer between the absorber layer and metal electrode in the CdTe solar cells, the back contact material (e.g., Sb_2Te_3) is generally an intermediate degenerated semiconductor, which increases the conductivity and creates a tunneling barrier. So we studied the electronic properties of Sb_2Te_3 thin films from the Hall measurements. Table 1 shows the parameters for Sb_2Te_3 thin films such as mobility, Hall coefficient, and carrier concentration. The thin films as-deposited and annealed at 613 K are p-type semiconductor compounds and have high carrier concentrations, 7.60×10^{19} and $5.87 \times 10^{19} \text{ cm}^{-3}$, respectively. Although the carrier concentration decreases slightly, the mobility of the Sb_2Te_3 thin films increases after the heat treatment, which means that the polycrystalline Sb_2Te_3 thin films have higher conductivity than amorphous ones and the thin films without Cu doping are suitable to form a p^+ -region layer to reduce the barrier height.

Meanwhile, electrical conductivity measurements were made on as-deposited Sb_2Te_3 thin films in the temperature range 300–650 K. The plot of conductivity versus temperature is shown in Figure 6. The conductivity decreases slowly with increasing temperature in the lower temperature range and reaches the minimum values at 433 K, and then it increases. This kind of change may be attributed to the oxidation of Te or Sb on the surface of the thin films as evidenced by the XRD and XPS studies. Above 473 K, however, the conductivity decreases at a rapid rate and subsequently increases after passing the minimum at a temperature of 523 K. It indicates that the films undergo a phase transition, from amorphous to crystalline between 473 and 523 K. This is consistent with XRD spectra (see Figures 1 and 2). Similarly, this irreversible behavior has also been observed on Sb-Te and Se-Te alloy systems [13, 14].

4. Conclusions

Sb_2Te_3 thin films were prepared by the vacuum coevaporation technique, together with posttreatment. As-grown thin films, which are oxidized easily in air, are an amorphous phase. After annealing the polycrystalline Sb_2Te_3 , thin films having a rhombohedra structure were obtained. An abnormal temperature dependence of conductivity was observed

in the temperature range 300–650 K, which shows that an amorphous-crystalline phase transition occurs in the thin films. Annealed at a high temperature can prevent effectively the oxidation of the thin films and increase obviously the mobility of thin films.

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