Research Article

Effect of Annealing on the Properties of Antimony Telluride Thin Films and Their Applications in CdTe Solar Cells

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Antimony telluride alloy thin films were deposited at room temperature by using the vacuum coevaporation method. The films were annealed at different temperatures in N_2 ambient, and then the compositional, structural, and electrical properties of antimony telluride thin films were characterized by X-ray fluorescence, X-ray diffraction, differential thermal analysis, and Hall measurements. The results indicate that single phase antimony telluride existed when the annealing temperature was higher than 488 K. All thin films exhibited p-type conductivity with high carrier concentrations. Cell performance was greatly improved when the antimony telluride thin films were used as the back contact layer for CdTe thin film solar cells. The dark current voltage and capacitance voltage measurements were performed to investigate the formation of the back contacts for the cells with or without Sb_2Te_3 buffer layers. CdTe solar cells with the buffer layers can reduce the series resistance and eliminate the reverse junction between CdTe and metal electrodes.

1. Introduction

CdS/CdTe thin film solar cells have attracted much technological interest due to their remarkably low cost and high conversion efficiency of 19.6% [1]. One of the key issues in CdTe solar cells is the high electron affinity; therefore, a high work function metal is required to form a good ohmic contact to p-type CdTe [2]. An approach to overcome this problem is to incorporate a buffer layer between the CdTe and the metal electrodes [2]; that is, materials doped with Cu or even a Cu layer have been used to form back contacts, such as ZnTe:Cu [3], Cu/Au [4], Cu/graphite [4], and Cu/Mo [5]. However, Cu will diffuse into the main junction and may influence the stability of the cells [6]. In order to form a stable and effective back contact, Romeo et al. [7, 8] fabricated CdS/CdTe solar cells using Sb_2Te_3 thin films as a back contact. These solar cells show the high efficiency of 14.6% and long-term device stability.

Different methods have been used to prepare Sb_2Te_3 thin films, such as physical vapor deposition [6], radio frequency magnetron sputtering [7], electrochemical deposition [9], thermal evaporation [10], and metal organic chemical

vapor deposition [11]. Arun and Vedeshwar [12] found that the resistance of the polycrystalline Sb_2Te_3 films strongly depends on the grain size and intergranular voids. Fang et al. [13] investigated the effects of annealing on thermoelectric properties of Sb_2Te_3 thin films. Hu et al. [14] studied the properties of CdTe/ Sb_2Te_3 interfaces and the role of Sb in CdTe solar cells.

In this work, Sb_2Te_3 thin films were prepared at room temperature by a vacuum coevaporation method, and the effect of annealing on the properties of thin films and performance of CdS/CdTe thin film solar cells were investigated.

2. Experimental Details

Antimony telluride thin films were deposited on glass substrates by the vacuum coevaporation method. The vacuum system had a base pressure of 6×10^{-4} Pa and the Te powder of 5 N (99.999%) purity and Sb ingot of 5 N (99.999%) purity supplied by Alfa Aesar (USA) were used as the starting materials. The Sb and Te deposition rates were measured by two LHC-2 quartz monitors. The as-deposited films were

annealed at different temperatures in N_2 ambient. The film thickness was measured by using a stylus surface profiler and the composition of the thin films was measured by X-ray fluorescence (XRF). The structure of the samples was investigated by X-ray diffraction (XRD), using $CuK\alpha$ ($\lambda = 0.154184$ nm) radiation. Dark conductivity was measured using a two-probe technology. The four-probe Van der Pauw method was used to carry out the Hall measurements to determine the mobility and carrier concentration. The as-deposited films were cleaved from the substrates; then the thermal effect was investigated by the way of differential thermal analysis (DTA) in N_2 ambient using a TG/DTA 6300 of Seiko Instruments SII. The gas rate was 100 mL/min, and the heating rate was 10 K/min.

CdTe-based solar cells of the superstrate configuration were fabricated. CdS and CdTe layers were sequentially deposited by chemical bath deposition and close-spaced sublimation on TCO-coated glass substrates. After deposition, the samples were submitted to a wet $CdCl_2$ treatment at 400°C in air for 30 min. Then an Sb_2Te_3 layer (~100 nm) was deposited using the vacuum coevaporation technique at room temperature on the CdTe surface which was previously etched with Br-methanol. These samples were subsequently annealed in N_2 ambient. Finally, Au was deposited by electron beam evaporation as the back electrodes. The typical structure of the cells was glass/TCO/CdS/CdTe/ Sb_2Te_3 /Au. The resulting photovoltaic devices were characterized using the light current voltage ($J-V$) measurement under simulated AM1.5 illumination (i.e., 1000 W/m²), dark $J-V$, and capacitance voltage ($C-V$) measurements.

3. Results and Discussion

Figure 1 shows the XRD patterns of 624 nm thick Sb-Te alloy thin as-deposited films. The Sb-Te alloy thin films are amorphous at room temperature. To determine the composition of the Sb-Te alloy thin films, XRF spectra of Sb-Te alloys were carried out. XRF of as-deposited Sb-Te alloy thin films is shown in Figure 2. By calculating the peak area of Sb $K\alpha$ (12.8°) and Te $K\alpha$ (13.4°), every square centimeter of Sb-Te film quality can be worked out to be 0.118 and 0.174 mg, respectively. Thus, the Te:Sb ratio is 1.41:1. Considering the errors caused by instruments and so on, these results are acceptable although the standard chemical ratio is 1.5:1. Therefore, the results show that the chemical composition of the thin films is Sb_2Te_3 .

Figure 1 also shows Sb-Te alloy thin films annealed at different temperatures in N_2 ambient, from which it indicates that the films are polycrystalline. As increasing the annealing temperature up to 439 K, the thin films contain three peaks. One diffraction peak of Sb_2Te_3 at the angle of 26.322° could be observed, while the other peaks are at angles of 28.671° and 39.709°, corresponding to the (106) and (1012) planes of Sb_7Te , respectively. When annealed at about 488 K, the pattern of the films is different from that of the films annealed at 439 K. The peaks of Sb_7Te are totally suppressed, and more diffraction peaks of Sb_2Te_3 , such as (006), (015), (1010), (0111), (0015), (0018), (0210), (1019), and (0120), emerge with the peak of Sb

FIGURE 1: X-ray diffraction patterns of Sb-Te thin as-deposited films and annealed at different temperatures in N_2 ambient.

at 23.688°. Peaks of Sb_2Te_3 (1013) and (0114) become more distinct and the phase of Sb disappears when the films are annealed at 533 K. The peaks of Sb_2Te_3 become significantly strong when the films are annealed at 583 K, and there are no other phases but Sb_2Te_3 . This indicates that annealing promotes the formation of single phase Sb_2Te_3 .

To explore the effect of annealing temperature on Sb-Te alloy thin films, DTA was performed. Figure 3 shows the differential thermal curve of as-deposited films. Unlike peaks of single crystal, whose reaction intervals were compressed into a small range, the peak of as-deposited Sb-Te alloy thin films was extended from 323 to 705 K. And it was hard to figure out the base line, either at the initial temperature or at the final temperature. The negative DTA values meant endothermic reactions happened while heating. At first, DTA decreased because Sb atoms and Te atoms moved into lattice sites so as to get crystallized. As shown in Figure 1, lattice constant transition took place in the Sb-Te alloy thin films while annealing, and it ended at 488 K. In addition, the decomposition of metastable Sb_7Te occurred at about 439 K; as the temperature was rising to about 533 K, this reaction was accomplished. Energy consumption also took place during these processes. These results were verified by the differential thermal curve shown in Figure 3, in which the DTA value became more and more negative till the temperature reached up to 517 K. After that, the DTA value elevated with increasing temperature, but it was still negative. This might be due to the fact that was the quantity of atoms that was involved in the relocation decreased and that implied that more and more atoms had moved to lattice sites then had been crystallized.

Based upon the results of DTA, X-ray diffraction patterns of the samples with different thicknesses annealed at 583 K were investigated as shown in Figure 4. Compared with

FIGURE 2: X-ray fluorescence of as-deposited Sb-Te alloy thin films.

FIGURE 3: Differential thermal analysis of Sb-Te alloy thin films.

the samples with variable thicknesses, it can be concluded that trigonal Sb_2Te_3 obtained at above 267 nm is superior to others. In addition, the preferred orientation is at 28.244° along the (015) planes and more peaks become distinct with the increase of thickness. Therefore, the results convincingly show that Sb_2Te_3 thin films can be prepared by coevaporation and annealing contributes to the grain growth.

As a buffer layer between the absorber layer and metal electrodes in the CdTe thin film solar cells, we investigated the electrical properties of Sb-Te alloy thin films by Hall measurements. Figure 5 shows the trends of Hall mobility and hole concentration against temperature. The carrier concentration of the order of 10^{19} cm^{-3} for the thin films was

FIGURE 4: X-ray diffraction patterns of the samples with different thicknesses annealed at 583 K.

obtained. The conduction type of the films was measured by the thermal probe method and the samples were proved to be all p-type conductors, which is consistent with the results of the Hall measurements. At the annealing temperature of 423 K the Hall mobility was rather small, only $8.86 \text{ cm}^2/\text{Vs}$.

FIGURE 5: Electrical properties of the thin films annealed at different temperatures.

As the annealing temperatures increased, the carrier concentrations did not alter dramatically, while the mobility increased rapidly, especially at the temperature in the range from 423 to 525 K. The impressive high values make it a promising back contact material for CdTe solar cells. The carrier mobility has the following relation:

$$\mu_p = \frac{q\tau_p}{m_p}, \quad (1)$$

where μ_p is the mobility, q is the electronic quantity, τ_p is the relaxation time, and m_p is the effective mass. Because the carrier effective mass did not alter much, it is deduced that the increase of the mobility is due to the decrease of the relaxation time, which inverses to the scattering probability. As-deposited Sb-Te alloy thin films were amorphous, in which defects commonly exist. The quantity of defects is large enough to disregard other scattering mechanisms such as sonic scattering one and optical scattering one at a certain temperature. That means carriers are mostly scattered by defects in the Sb_2Te_3 thin films. After annealing, the number of defects is reduced significantly. Thus the scattering probability is also decreased, and the mobility is elevated. This is consistent with the results of XRD patterns as shown in Figures 1 and 4, in which the transition of Sb-Te alloy thin films from the amorphous Sb-Te phase into polycrystalline Sb_2Te_3 in the temperature range of 423–525 K is shown.

Meanwhile, the electrical conductivity of the as-deposited Sb-Te alloy thin films was surveyed in the temperature range from 300 to 623 K. The conductivity versus temperature plot is shown in Figure 6. The conductivity increases slowly with the increasing temperature. Then it increases dramatically in the temperature range about 385–455 K. However, the conductivity slight alteration occurs as the temperature is higher than 455 K. This kind of alteration can be attributed to the phase transition for the as-deposited films from the amorphous Sb-Te phase into mixtures phases of polycrystalline Sb_2Te_3 and Sb_7Te_3 as evidenced by XRD and DTA

FIGURE 6: The temperature dependence of dark conductivity for Sb-Te alloy thin films.

investigations. This phenomenon was also observed by El Mandouh [15].

The aim of this work is to investigate the potential of antimony telluride films for solar cell applications. Thus, antimony telluride thin films were used as a back contact layer for CdS/CdTe solar cells. Before the deposition of antimony telluride films on the CdTe layer, an etching process was required. And then antimony telluride thin films were deposited. Finally the cells were annealed from 523 to 623 K based upon the studies mentioned above. Table 1 shows photovoltaic parameters for CdS/CdTe solar cells with or without antimony telluride buffer layers at different annealing temperatures. Obviously, cell performance in CdTe solar cells with Sb_2Te_3 is superior to those without the buffer layers. Sb_2Te_3 as the back contact layer of solar cells contributes to the improvement short circuit current (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF).

To further study the function of Sb_2Te_3 layers in back contact formation, the dark J - V and C - V characteristics for CdTe solar cells were measured (Figures 7 and 8). Figure 7 shows the dark J - V curves of CdTe solar cells with or without Sb_2Te_3 back contact layers. Curve (a) reaches saturation when the voltage is higher than open circuit voltage, that is, rollover occurs. In contrast to curve (a), curve (b) increases with the elevating voltage. It can be assumed that the main reason devoted to the roll-over phenomenon is the high series resistance. Therefore, Sb_2Te_3 back contact layers can effectively improve the contact characteristics and reduce the series resistance.

Figure 8 shows the capacitance voltage curves of CdTe solar cells with/without Sb_2Te_3 back contact layers. One can see that curve (a) is upward when the external bias potential is 1.8 V or larger, while curve (b) is, on the contrary, straightly downward all the way. From these results we conclude that the reverse junction comes into being between the metal electrodes and p-type CdTe without Sb_2Te_3 back contact layers. And it is successfully eliminated when Sb_2Te_3 back contacts are deposited. The carrier concentrations from the two curves were obtained, curve (a) showing a result of

FIGURE 7: Dark J - V curves for CdTe solar cells with Sb_2Te_3 (a) or without the back contact layer (b).

FIGURE 8: $1/C^2$ - V curves for CdTe solar cells with Sb_2Te_3 (a) or without the back contact layer (b).

TABLE 1: The parameters for CdS/CdTe solar cells with or without Sb_2Te_3 back contacts at different annealing temperatures.

Temperature	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	E_{ff} (%)
Without back contacts	720.9	20.3	54	7.9
No annealing	680.1	19.2	50	6.53
523 K	743.7	23.5	55	9.61
573 K	805.9	25.1	61	12.34
623 K	784.9	24.3	58	11.06

$3.89 \times 10^{13}/\text{cm}^3$ while curve (b) $1.74 \times 10^{14}/\text{cm}^3$. Obviously, the order of magnitude of carrier concentration can be increased when the Sb_2Te_3 back contacts was adopted.

4. Conclusions

Antimony telluride thin films were deposited at room temperature by the vacuum coevaporation method, and the results show that single Sb_2Te_3 phase exists when the annealing temperature is higher than 488 K. The Hall mobility of

Sb_2Te_3 increases with the elevating annealing temperatures, while the carrier concentration decreases. With the application of a back contact material in CdTe thin film solar cells, we can effectively improve the short circuit current, open circuit voltage, and fill factor, thus greatly improving the conversion efficiency. The results also show that antimony telluride films can improve the contact characteristics between CdTe and the back electrodes, reduce the series resistance, and eliminate the effect of the reverse junction.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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