Research Article

The Structure and Stability of Molybdenum Ditelluride Thin Films

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Molybdenum-tellurium alloy thin films were fabricated by electron beam evaporation and the films were annealed in different conditions in N_2 ambient. The hexagonal molybdenum ditelluride thin films with well crystallization annealed at 470°C or higher were obtained by solid state reactions. Thermal stability measurements indicate the formation of MoTe_2 took place at about 350°C , and a subtle weight-loss was in the range between 30°C and 500°C . The evolution of the chemistry for Mo-Te thin films was performed to investigate the growth of the MoTe_2 thin films free of any secondary phase. And the effect of other postdeposition treatments on the film characteristics was also investigated.

1. Introduction

Molybdenum ditelluride (MoTe_2) belongs to the large family of layered transition metal dichalcogenides, which is bound by weak van der Waals interactions along the c -axis [1]. The electronic, optical, magnetic, and catalytic properties of the transition metal dichalcogenides have been extensively studied [2–6]. MoTe_2 can act as an efficient absorbing layer in solar cells only if the crystallites of the films are textured with the c -axis perpendicular to the plane of the substrate [7]. Because of the layered structure of MoTe_2 , various metal atoms can be doped between the layers to change its optical and electrical properties [8]. It has been found that H absorption on MoTe_2 monolayers results in large spatial extensions of spin density and weak AFM coupling between local magnetic moments even at the distance of above $12.74 \text{ \AA}$ [4]. MoTe_2 has a bandgap of around 1.1 eV and a high work function of $\sim 4.7 \text{ eV}$, and the valence band offset of $\text{CdTe}/\text{MoTe}_2$ is only 0.03 eV [1]; these are advantageous to the hole transport between cadmium telluride and molybdenum ditelluride. Therefore, MoTe_2 is a potential candidate for a stable Cu-free back contact to CdS/CdTe solar cells.

Tellurium pressure or vapor is often indispensable for the preparation of the MoTe_2 thin films [9, 10], and the adhesion or reproducibility of the films is very poor. In this work,

MoTe_2 thin films were synthesized by solid state reactions between Mo and Te thin films followed by an anneal in N_2 ambient. The structural property and stability of Mo-Te thin films were investigated under different postdeposition treatment conditions.

2. Experimental

Molybdenum-tellurium alloy thin films were deposited by electron beam evaporation at room temperature in the pressure of $\sim 10^{-4} \text{ Pa}$. The multilayer Mo/Te films with a stacking sequence Te-Mo-Te-Mo were deposited independently and alternately using high purity molybdenum (99.999% purity, Alfa Aesar) and tellurium (99.999% purity, Alfa Aesar). The deposition rates of molybdenum and tellurium were monitored by a thickness monitor. The total thickness of the molybdenum-tellurium multilayer thin films was $200 \sim 450 \text{ nm}$. After deposition, a posttreatment was performed at different temperatures in N_2 ambient. The temperatures reproducible to $\pm 1 \text{ K}$ were obtained from repeated runs on the same sample.

The structure and the surface morphology of the samples were done by X-ray diffraction (XRD) (DX-2600, Dandong, China) and atomic force microscope (AFM) (MFP-3D-BIO,

FIGURE 1: XRD patterns of Mo-Te thin films annealed at different temperatures for 15 min in N_2 ambient.

Asylum Research, USA). The film thickness was surveyed using a stylus profiler (XP-2, Ambios Technology Inc., USA). To study the effect of annealing on the $MoTe_2$ thin films, thermogravimetry and differential scanning calorimetry (TG/DSC) (STA 449C, NETZSCH, Germany) analysis were carried out. X-ray photoelectron spectra (XPS) (ESCALAB 250, Thermo Fisher SCIENTIFIC, UK) were performed to determine the atom chemical states.

3. Results and Discussion

Figure 1 shows the XRD patterns of the Mo-Te thin films with 450 nm thickness annealed at different temperatures in N_2 ambient. The peaks marked by rhombus were indexed to the phase of Te (JCPDS NO. 65-3370), and the others were the phase of $MoTe_2$ (JCPDS number 15-0658) (see Figure 1). The reflection positions in the XRD patterns of as-deposited layers were at the angles of 23.029° , 27.560° , 40.454° , and 49.650° , which correspond to Te (100), (011), (110), and (021). In order to form the crystalline compound $MoTe_2$ thin films with a simple hexagonal Bravais lattice, thermal postdeposition treatment was performed. The as-deposited thin films were annealed at $300^\circ C$, $356^\circ C$, $450^\circ C$, $470^\circ C$, and $475^\circ C$ in N_2 ambient, respectively. After annealing at $300^\circ C$ in N_2 ambient, many more diffraction peaks of Te, such as (012), (111), and (200), emerged at 38.263° , 43.353° , and 47.060° . When the annealing temperature reached $356^\circ C$, the patterns of the films were very different from those of

the films annealed at $300^\circ C$; the peaks corresponding to $MoTe_2$ (002) and (004) were revealed by XRD patterns as shown in Figure 1. It was noticed that two diffraction peaks of Te (011) and (112) were also observed in the XRD patterns. The results show that a considerable amount of Te and Mo diffuses into the Mo and the Te films, respectively. The chemical reaction that took place in the thin elemental layers can be described as $2Te + Mo \rightarrow MoTe_2$. The thin films with well crystallization were achieved when annealing was performed at $470^\circ C$ or higher. The peaks of $MoTe_2$ (006) could be observed at 38.905° , and there were no peaks of Te. These results indicate the disappearance of Te but the presence of $MoTe_2$ with increasing the annealing temperature. Therefore, annealing promotes the formation of $MoTe_2$ and annealing at $470^\circ C$ leads to the single phase $MoTe_2$ thin films.

To study the stability of the molybdenum-tellurium alloy thin films, TG and DSC analysis were performed. The thin films as-deposited were cleaved from the substrates; approximately 2.952 mg of sample was used in this work. The gas rate was 30 mL/min, and the heating rate was 10 K/min. Figure 2 shows the TG-DSC curves of as-deposited films. The peaks of as-deposited $MoTe_2$ thin films were extended from $30^\circ C$ to $600^\circ C$. The peaks in DSC values meant endothermic reactions happened while heating. The first endothermic peak was located at $68.5^\circ C$ and it was the endothermic peak of water. Then with the increase of temperature, there were endothermic peaks appearing at about $350^\circ C$ and $448.5^\circ C$ due to the energy consumption, which results from Te atoms and Mo atoms moving into lattice sites so as to form

FIGURE 2: TG and DSC analysis of the as-deposited films.

MoTe₂. This behavior is consistent with the results of XRD (Figure 1); that is, polycrystalline MoTe₂ was gradually formed when the annealing temperature increased up to 350°C. From the TG values also shown in Figure 2, one can see that there was almost no weight loss at the temperatures lower than 500°C, whereas the TG curve dropped sharply at the temperatures higher than 500°C. The severe weight-loss might be the reevaporation of tellurium for MoTe₂, the results of which will be discussed later.

With the increase of the annealing temperature, the intensities of the peaks for the thin films became significantly strong and the positions of the peaks were not changed (Figure 3). These indicate the improved crystallinity and stable structure of MoTe₂ thin films due to the interdiffusion. As the annealing temperature increased up to 500°C, although the weight-loss was about 2% (Figure 2), an amorphous baseline distinctly appeared. We attribute the poor crystallinity of the films to the severe reevaporation of tellurium in the process of the postdeposition treatments. When the annealing temperature was further increased, the adhesion of the films was poor. Grain growth of MoTe₂ thin films may introduce stress at the glass/MoTe₂ interface, resulting in film blistering or peeling.

Based upon the investigations of XRD and TG/DSC analysis, the evolution of the morphology and chemistry for MoTe₂ thin films annealed at temperatures lower than 500°C was studied by AFM and XPS (Figures 4-5). Figure 4 shows the atomic force microscopy of Mo-Te thin films as-deposited and annealed at 475°C in N₂ ambient. The surface of the as-deposited MoTe₂ thin film was smoother than the one annealed at 475°C. The root mean square of the as-deposited film was 1.179 nm while it became 19.803 nm after annealing. That means annealing could promote the growth of the grains. The well-distributed atoms moved to lattice sites so the valleys and peaks on the surface were detected by AFM, and this is consistent with the XRD results.

Figure 5 shows XPS spectra of Mo-Te thin films at different temperatures. When the annealing temperature was

FIGURE 3: XRD patterns of Mo-Te thin films with a thickness of 450 nm annealed at 485°C, 495°C, and 500°C for 15 minutes in N₂ ambient.

below 450°C, it was noticed that there was only one emission peak in XPS spectra of Mo 3d_{3/2}, which drew core level lines at about 232.75 eV, and it was a double peak. The emission peak with lower binding energies was determined to be the Mo 3d_{5/2} in MoTe₂ which occurred at 229.2 eV when the annealing temperature reached 450°C or higher. That means MoTe₂ was formed when the annealing temperature rose to 450°C and it has been confirmed by XRD in Figure 1. In Figure 5, the doublet of Te 3d was doubled (the two Te 3d_{5/2} peaks being at about 572.9 eV and 576.5 eV), while the Te 3d_{5/2} position of TeO₂ occurred at 576 eV; maybe there was a small amount of tellurium oxidation at the surface of the films. It was obvious that the ratio of ionized Te/elemental Te increased dramatically after annealing since the peak area was proportional to the chemical composition. The results show

FIGURE 4: AFM images of Mo-Te thin films as-deposited (a) and (b) annealed at 475°C for 15 min in N₂ ambient.

FIGURE 5: XPS spectra of (a) Mo 3d, (b) Te 3d, and (c) O 1s for Mo-Te thin films annealed at different temperatures.

FIGURE 6: XRD patterns of Mo-Te thin films with thickness of 450 nm annealed at 470°C for different times in N₂ ambient.

that a large amount of Te was not alloyed in the as-deposited films. After annealing, most of Te was alloyed with Mo in the form of MoTe₂ due to the interdiffusion. This could explain why the peak of Te was firstly detected but disappeared after annealing in XRD patterns (see Figure 1).

To further explore the effect of annealing on the structure of Mo-Te thin films, the other thermal postdeposition treatments such as annealing time and thickness were carried out. Figure 6 shows XRD of Mo-Te thin films with thickness of 450 nm annealed at 470°C for different annealing time. It was noticed that when the annealing time was 10 minutes, peaks of MoTe₂ (002), (004), (006), and (008) were revealed with Te (100) at 23.029°, while the annealing time reached 15 minutes and the Te phase disappeared. With the increase of the annealing time (e.g., 20 minutes), the crystallization of the films was not better than that of the films annealed for 15 minutes and the intensities of the peaks became weak.

FIGURE 7: XRD patterns of Mo-Te thin films annealed at 470°C in N₂ ambient with different thicknesses.

The poor crystallization can be also attributed in part to the reevaporation of tellurium.

From Figure 7, peaks of Te (100), (110), (111), (200), (021), and (210) for 300 nm thick Mo-Te thin films were detected with MoTe₂ (002). As the film thickness increased to 400 nm, the number of diffraction peaks of Te was suppressed and the peak of MoTe₂ (004) was firstly observed. With the increase of the thickness for the thin films, more peaks of single phase MoTe₂, such as (006) and (008), were detected in the 450 nm thick Mo-Te thin films.

4. Conclusions

Mo-Te thin films were deposited at room temperature by electron beam evaporation, and then the films were annealed in N₂ ambient under different conditions. The formation of

MoTe₂ thin films took place at about 350°C and the structure of the thin films was stable from room temperature to 500°C. As the temperature increased, the growth of the MoTe₂ phase was predominated and the Te secondary phase was suppressed. The thin films were single phase MoTe₂ and well crystallized in the hexagonal structure annealed at 470°C or higher. At a temperature of 500°C or higher, or even for a long annealing time, the thin films were poor due to the reevaporation of tellurium and the adhesion-loss problems.

Conflict of Interests

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

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