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Abstract

Bi_{0.5}Sb_{1.5}Te₃ thin films were deposited on glass substrates by pulsed laser deposition (PLD) method at room temperature. Annealing effect on properties of the films was studied by structural, morphology and physical characterizations. It was found that the as-grown amorphous film crystallizes at annealing temperature of 473 K. A semiconductor-metal transition was observed in annealed films. A linear magnetoresistance (MR) was investigated in the annealed films in a magnetic field up to 13 T without saturation at low temperature.

Keywords

thin, films, glass, type, pulsed, p, laser, deposition, properties, transport, magneto, fabrication, bi_{0.5}, sb_{1.5}, te₃

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Fabrication and Magneto-Transport Properties of p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Thin Films on Glass by Pulsed Laser Deposition

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$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films were deposited on glass substrates by pulsed laser deposition (PLD) method at room temperature. Annealing effect on properties of the films was studied by structural, morphology and physical characterizations. It was found that the as-grown amorphous film crystallizes at annealing temperature of 473 K. A semiconductor-metal transition was observed in annealed films. A linear magnetoresistance (MR) was investigated in the annealed films in a magnetic field up to 13 T without saturation at low temperature.

Keywords: Bismuth Doped Antimony Telluride, Magneto-Transport, Thin Film, Pulsed Laser Deposition.

1. INTRODUCTION

Thermoelectric materials are widely used in applications including temperature sensors, power generation and refrigeration devices.^{1,2} V–VI compounds, such as Sb_2Te_3 , Bi_2Te_3 , Bi_2Se_3 and their solid solutions, are well-known candidate materials for their room-temperature thermoelectric property due to their high figure of merit ($ZT = S^2T/\rho\kappa$), where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity and T is the temperature. Much effort has been made to raise the ZT of these compounds by doping and alloying with other elements. However, the ZT is not much improved and remains about 1, which seems reaching the limit for the bulk materials.³ Recently, enhanced thermoelectric properties were achieved in low-dimensional thermoelectric materials, which have brought considerable attention. It is believed that power factor can be increased by high electronic density of state near Fermi level in low-dimensional structure. In addition, thermal conductivity can be suppressed by phonon-boundary scattering and modification of phonon dispersion. As a result, ZT of low-dimension structures can be improved.

$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ has been proven a p -type thermoelectric compound with $ZT \approx 1$ at room temperature. The crystal structure composes of atomic layers in the order of Te(1)-Sb-Te(2)-Bi-Te(1) layers oriented along the c -axis. The Te layers stacks to each other by weak van der

Waals force. Very recently, advanced synthesis methods, including direct current magnetron sputtering⁴ and flash evaporation,⁵ have been used to prepare $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ low-dimensional thin films in order to improve the figure of merit. By far, most $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films were prepared on crystallized substrates at high temperature. It is still challenging to deposit $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin film on amorphous substrates at low temperature. In addition, the resistance behaviours of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films in present of magnetic fields are still unclear.

In this paper, $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films are fabricated by pulsed laser deposition method. The optimal synthesis conditions have been studied. The crystal structure, morphology, thermoelectric properties and electrical properties have been systematically investigated. In particular, the magnetoresistance of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ has been studied in wide range of temperature and magnetic field.

2. EXPERIMENTAL DETAILS

$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films were deposited on glass substrates by using a PLD system. A commercial p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ polycrystal pellet was used as the target. The pellet was 28 mm in diameter and 10 mm in thickness. The target was loaded in a stage that was rotated about the normal to the surface. The glass substrate was mounted in the stainless-steel vacuum chamber. The deposition chamber was evacuated to 2×10^{-2} Torr by vacuum pump. The temperature of substrate was room temperature. Third harmonic generation of a Nd:yttrium aluminium garnet laser

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Fig. 1. XRD patterns of *p*-type Bi_{0.5}Sb_{1.5}Te₃ film deposited on glass substrate with different annealing temperatures.

with a wavelength of 355 nm and a repetition rate of 10 Hz was used as the laser source. The laser beam was incident on the target at 45°. The deposition time was 10 mins. After deposition, the thin films were annealed in tube furnace under Ar atmosphere for 1 hour at various temperatures from 473 K to 623 K.

Crystal structures of all samples were studied by XRD over the 2θ range from 6° to 65°, which were obtained by a GBC-MMA diffractometer using Cu K α radiation ($\lambda = 1.54059$ Å). All X-ray analyses were performed with 0.02° step size and 2°/min scanning speed. The growth morphology of thin films was examined by scanning electron microscopy (SEM, JSM-6460). The electrical resistivity and magnetoresistance were examined on a commercial physical properties measurement system (14 T PPMS, Quantum Design).

3. RESULTS AND DISCUSSION

The XRD patterns of Bi_{0.5}Sb_{1.5}Te₃ films deposited by PLD with different annealing temperatures are shown in Figure 1. A bump background in all XRD patterns attribute to amorphous glass substrate. As observed in XRD pattern, the as-grown Bi_{0.5}Sb_{1.5}Te₃ thin films exhibit amorphous structure. It was found that Bi_{0.5}Sb_{1.5}Te₃ thin films crystallize in rhombohedral structure with the space group $D_{3d}^5(R\bar{3}m)$ after annealing. The samples were found well crystallized with annealing temperature of 523 K. The films were molten when the annealing temperature above 623 K. Three peaks were observed in as-grown Bi_{0.5}Sb_{1.5}Te₃ XRD pattern. It indicates that the sample has amorphous structure due to broad peaks with low

Fig. 2. Surface morphologies and cross-section SEM images of *p*-type Bi_{0.5}Sb_{1.5}Te₃ thin films deposited on the glass substrates. (a) as-grown, (b) annealed at 523 K, (c) annealed at 573 K, (d) annealed at 623 K.

Fig. 3. Temperature dependences of the electrical resistivity of p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films with different annealing temperatures.

diffraction intensity. New peaks emerge in XRD patterns after annealing at 523 K, including these at peak positions of 28° , 39° , 42° and 52° . They correspond to $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ crystal orientations of (015), (1010), (110) and (205) planes, respectively. It indicates that the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films are fully crystallized at 573 K. Further annealing at 623 K results in even better crystalline of the films.

The sharp and strong peaks of (015) and (110) show the preferred crystallized orientations of the films. Annealing process can enhance crystalline of samples by removing the defects such as voids, grain boundaries, dislocations, stress, etc., which in turn improves the electrical properties of the films. It is believed that the 573 K annealing process can enhance the crystalline of the films, and eventually, improve the physical properties of the films.

SEM images of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films with different annealing temperatures are shown in Figure 2. The as-grown film shows a smooth surface with sub-micron droplets and large particulates. The dimension of these particulates-shape-like flat disks is $4\text{--}5\text{ }\mu\text{m}$. Very few particulates can be observed in as-grown films because lower laser fluencies have been utilized during the deposition.⁶ When the annealing temperature is increased to 523 K, 573 K and 623 K, the surface morphology is found rougher in comparison to the as-grown sample. It can be attributed to diffusion of volatile Sb in the annealing process. The annealing process possibly induces the deformation of thin film surface resulting in the structural defect, as shown in Figure 2. However, further study is necessary to investigate this phenomenon in the further work.

Fig. 4. The field dependence of the transverse magnetoresistance measured from 5 K to 200 K for p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin film on glass after annealing at (a) 473 K, (b) 523 K, (c) 573 K and (d) 623 K. The electric current was applied perpendicular to the magnetic field.

The temperature dependences of resistivity for Bi_{0.5}Sb_{1.5}Te₃ thin films were measured in temperature range from 5 K to 300 K, which is plotted in Figure 3. All samples exhibit an increase in resistivity when the temperature decreases from 300 K to 5 K. The resistivity of 523 K and 573 K annealed films are quasi constant, which are $\sim 5 \text{ m}\Omega \cdot \text{cm}$ and $\sim 6 \text{ m}\Omega \cdot \text{cm}$, respectively. As the annealing temperature changes from 523 K to 623 K, the resistivity of thin films increases accordingly. The 473 K annealed film exhibits a metal-semiconductor transition at $\sim 70 \text{ K}$. The sample with annealed temperature of 673 K exhibits semiconductor behaviour.

Positive magnetoresistance was observed in the Bi_{0.5}Sb_{1.5}Te₃ film annealed at 473 K, 523 K, 573 K and 623 K. We measured the magnetic field dependence of the resistance over a wide range of temperature from 5 K up to 200 K. Transverse magnetoresistance was measured in a magnetic field perpendicular to the direction of current. The MR ratio is defined as $[(\rho_H - \rho_0)/\rho_0] \times 100\%$, where ρ_H and ρ_0 are the resistance with and without the magnetic field H , respectively. For all thin films, the MR ratio is positive and symmetrical. The films exhibit superlinear magnetic field dependence above 50 K. The sublinear magnetic field dependence at 5 K is observed in the samples annealed at 473 K, 573 K and 623 K. Linear magnetoresistance was observed at 5 K over decades in field in 523 K annealed sample. The MR ratios increase with decreasing temperature. The largest MR ratio values for the samples annealed at 473 K, 523 K, 573 K and 623 K are 5.07%, 7.88%, 3.37% and 10%, respectively at 5 K. Bi_{0.5}Sb_{1.5}Te₃ is a compound with a gapless band structure, which is significantly sensitive to the external influences, including thermal, magnetic and electric fields. As has been reported before, the Fermi level in gapless compounds is believed to penetrate into conduction/valence

bands in the presence of thermal influences.⁷ In addition, Hall mobility possibly increases as the annealing temperature increased although the hole concentration also increased. It will induce unusual behaviour as the scattering probability increases due to the introduction of defects. As a result, a great magnetoresistance was observed in all Bi_{0.5}Sb_{1.5}Te₃ thin films.

4. CONCLUSION

Bi_{0.5}Sb_{1.5}Te₃ thin films were deposited on amorphous glass substrate by PLD technique. Annealing process played an important role in enhancing the crystalline and surface morphologies of the films. Thin films annealed above 473 K exhibit semiconductor-like resistance at low temperature. A large magnetoresistance of the films were observed which is attributed to the gapless band structure of the compound.

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