Journal of Alloys and Compounds 702 (2017) 229–235

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Combined infrared spectroscopy and first-principles calculation analysis of electronic transport properties in nanocrystalline Bi_2Te_3 thin films with controlled strain

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A R T I C L E I N F O

Article history:
Received 5 November 2016
Received in revised form
9 January 2017
Accepted 18 January 2017
Available online 20 January 2017

Keywords:
Infrared spectroscopy
First-principles calculation
Electronic transport properties
Bi_2Te_3
Strain
Nanocrystalline

A B S T R A C T

The carrier concentration and mobility in nanocrystalline Bi_2Te_3 thin films with controlled strain were investigated through a combination of infrared spectroscopy and first-principles calculations, and the results were compared to Hall measurement data. The thin films were deposited on flexible polyimide substrates using radio frequency magnetron sputtering at a substrate temperature of 200 °C. Various compressive strains were introduced into the thin films by changing the curvature of the flexible substrate prior to deposition. The magnitude of the strain was determined by X-ray diffraction, which found that the strain in the *c*-axis direction was more greatly influenced by the magnitude of curvature than that in the *a,b*-axis direction. The average crystallite size remained at ~30 nm across the entire range of strains tested, but did slightly increase with decreasing strain. The electronic transport properties were estimated by infrared spectroscopy using the Drude model, with the effective mass being determined from the band structure using first-principles calculations based on density functional theory. This combined analysis exhibited a similar decrease in carrier concentration and increase in mobility with decreasing strain as the Hall measurements, though the difference between the results of the two measurement methods became greater as the strain decreased.

1. Introduction

Applying strain to a material is an effective method of improving its electronic transport properties. Strained Si, for example, exhibits a high mobility due mainly to a decrease in its effective mass [1,2], and strained Si MOSFETs have been used commercially in high-grade processors [3]. The performance of thermoelectric materials is also improved by the application of strain [4], particularly when it comes to their electronic transport properties. This includes their carrier concentration and mobility, both of which are related to the electrical conductivity [5], as well as their Seebeck coefficient [6,7] and thermal conductivity [8,9]. The performance of thermoelectric materials is directly dependent on their dimensionless figure of merit ZT, which is defined as $ZT = S^2\sigma T/\kappa$, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. An investigation into the effects of strain on the electronic transport properties is therefore quite important to improving the thermoelectric performance.

Several types of strained thermoelectric materials have been developed, including superlattices [10,11], high-pressure materials [6,12], stretched or bent materials [13,14], and ion or electron beam irradiated materials [15,16]. The relationship between the magnitude of strain and electronic transport properties of such materials is normally estimated using bent thin films on a flexible substrate, as this allows the magnitude of the strain to be easily tuned by changing the bending curvature. In a previous study, it was demonstrated that the thermoelectric properties of bismuth telluride (Bi_2Te_3) thin films change upon bending of their flexible substrate [17], but the relationship between the strain and electronic transport properties remained unclear. However, it is known that strain affects energy band structures [18,19], and any variation in the band structure has an influence on the electronic transport properties. Electronic transport properties are generally measured via Hall measurements using the van der Pauw method, but precise measurements are difficult to obtain with bismuth telluride based alloys because of the relatively low Hall voltages generated by their high carrier concentration (10^{19}-10^{20} cm^{-3}). Noise is also

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http://dx.doi.org/10.1016/j.jallcom.2017.01.194
0925-8388/

generated in their Seebeck voltage generating by temperature differences due to the Peltier effect caused by a flowing electrical current.

Infrared spectroscopy can be used to estimate the carrier concentration and mobility of a material from its free-carrier absorption using the Drude model [20–22]. This method is convenient because it is independent of the shape of the sample and provides a non-contact technique. This method requires determining the effective mass from the energy band of a small region around the band extrema [23], and so the electronic transport properties can only be estimated by a combined analysis of infrared spectroscopy and first-principles calculation. In this study, radio frequency (RF) magnetron sputtering is used to prepare nanocrystalline Bi_2Te_3 thin films on polyimide substrates with various compressive strains generated by changing their curvature. The electronic transport properties of these strained Bi_2Te_3 thin films are then analyzed by combined analysis and compared against conventional Hall measurements to evaluate the effectiveness of these two estimation methods.

2. Experimental details

N-type Bi_2Te_3 thin films were deposited by RF magnetron sputtering (Tokuda, CFS-8EP) onto polyimide film substrates (size: 100 mm × 20 mm, 125 μm thick), which were selected for their high flexibility and heat resistance. The sputtering target was 127 mm in diameter and 5 mm thick, and composed of high-purity (99.9%) Bi–Te (32–68 at.%) sourced from Kojundo Chemical Laboratory Co., Ltd. This atomic composition made it possible to deposit thin films with a mostly stoichiometric atomic composition (i.e., 40 at.% Bi and 60 at.% Te). The distance between the substrate and target was set at 140 mm, and the substrate temperature was kept at 200 °C. Sputtering was performed in Ar gas (99.995%) at a pressure of 1.0 Pa. An RF power of 200 W and a deposition time of 1 h were used for all samples. To ensure a uniform film thickness, the substrate holder was rotated at 20 rotations per minute. Following deposition, the film thickness of all samples was confirmed to be ~1.0 μm.

To apply strain to the Bi_2Te_3 thin films, the polyimide substrates were bent in advance to the desired convex shape. The substrates were tightly bound to a flexible stainless steel plate used to attach them to a substrate holder, which maintained them at a constant temperature of 200 °C without affecting their curvature. Compressive strains were achieved by flattening the resulting films, i.e., by changing their bending radius back to zero from 10 to 42 mm. Tensile strain was not explored in this study due to the shrinkage of the substrate during the heating needed for film deposition [24].

The structural properties of the Bi_2Te_3 thin films were determined by X-ray diffraction (XRD; Mini Flex II, Rigaku), with the diffraction angle of the XRD peaks at (0 1 5) and (1 0 10) being subsequently used to calculate the lattice parameters. The crystallite size was estimated from the full-width at half-maximum values of the (0 1 5) XRD peaks using Scherrer's equation. For infrared optical measurement, Fourier transform infrared spectroscopy (FT-IR; FT/IR-4200, JASCO) was conducted at RT using the attenuated total reflectance method over a wavelength range of 1200–4000 cm^{-1} with a resolution of 1 cm^{-1}. Hall measurements were performed at RT using the van der Pauw method (HM-055, Ecopia) to estimate the carrier concentration, n. The electrical conductivity, σ, was measured at RT using a four-point probe method (RT-70V, Napson). As the mobility, μ, is expressed as $\mu = \sigma/ne$, the electrical conductivity was divided between the carrier concentration and the charge on the electron.

3. Calculation details

The band structures of the strained Bi_2Te_3 were obtained within the framework of density functional theory (DFT). The crystal structure of Bi_2Te_3 is rhombohedral, with a space group of $D^5_{3d}(R\overline{3}m)$ and five atoms in its trigonal unit cell [25]. This structure consists of quintuple layers of atoms stacked along the c-axis, and is most easily visualized in terms of its layer structure and hexagonal cell shown in Fig. 1. The five individual atomic layers that make up the quintuple layer occur in the sequence: $Te^{(1)}$–Bi–$Te^{(2)}$–Bi–$Te^{(1)}$, where $Te^{(1)}$ and $Te^{(2)}$ denote the two different types of tellurium atom that exist in the crystal. This description of the quintuple layer stacking is justified by the appreciable distance between adjacent $Te^{(1)}$ layers. Each atom is surrounded by three atoms in the layer below and three in the layer above, with a near-octahedral coordination along the c-axis. The exception to this is the $Te^{(1)}$ atoms, whose three nearest-neighbor $Te^{(1)}$ atoms are located on a different ‘quintuple’ layer leaf, and so are somewhat further away from being an octahedral coordination.

Calculating the band structure requires determining the experimental lattice parameters of the Bi_2Te_3 thin films from the XRD analysis, though for the sake of simplicity, the computational relaxation of internal atomic positions was omitted [5]. The DFT calculations were performed using the ABINIT package [26] with a plane-wave basis set and norm-conserving pseudopotentials. The exchange-correlation part of the Hamiltonian was represented by the local density approximation (LDA) [27] with Hartwigsen-Goedecker-Hutter data [28]. The spin-orbit term was included in the Hamiltonian as part of the self-consistent treatment. The cut-off energy of the plane-wave was set at 40 hartree, and the Brillouin zone was sampled using a fine mesh of 24 × 24 × 24 k-points. A trigonal lattice consisting of only five atoms contained in a primitive unit cell was used, with which the fractional coordinates for the Bi and Te atoms were determined as 0.400 and 0.212, respectively [29].

4. Results and discussion

4.1. Crystallographic properties of strained Bi_2Te_3 thin films

All of the peaks in the X-ray diffraction patterns of the Bi_2Te_3 thin films with different strains shown in Fig. 2 correspond to the reflections of the rhombohedral phase of Bi_2Te_3 (JCPDS 15–0863), indicating that there was no structural transition to another phase. The highest peak was that of (0 1 5) and the crystal orientation was largely the same in all the samples. The crystallographic properties of the Bi_2Te_3 thin films listed in Table 1 reveal that the lattice parameter of the c-axis is more influenced by the magnitude of the bending radius than that of the a,b-axis.

The relationship between the strain in the c-axis direction and that in the a,b-axis direction is presented in Fig. 3. Here, the strain is defined as the ratio of the lattice parameter for the thin film to that of the standard data for Bi_2Te_3 (JCPDS 15–0863). In both the c-axis and a,b-axis directions, the lattice strain can be defined as: (c-axis) = $(c-c_0)/c_0$ and (a,b-axis) = $(a-a_0)/a_0$, where c and a are the c-axis and a,b-axis lattice parameters of the samples, respectively, and c_0 and a_0 are provided by the standard data. Note that bending the substrate to a radius of 10–42 mm prior to depositing the thin film changes the strain in the c-axis direction from −0.6 to −2.8%, whereas that in the a,b-axis direction remained at between −0.1 and −0.4%. In other words, the strain in the c-axis direction is more greatly affected. This is possibly because Van der Waals bonding exists in the c-axis direction, whereas the bonding in the a,b-axis direction is mainly covalent with a small ionic contribution. Subsequent focus was therefore on the strain in the c-axis direction,