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Characteristics of nanostructured bismuth telluride thin films fabricated by oblique deposition

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ABSTRACT

Oblique angle deposition can reduce ion bombardment and facilitate precursor migration on surfaces, which can affect the crystallographic properties of thin films. We prepared nanostructured Bi_2Te_3 thin films by oblique deposition at room temperature, and analyzed their structural and thermoelectric properties. The thin films were deposited by radio-frequency magnetron sputtering on a glass substrate, which was tilted at angles of 0–80° to the target. Cross-sectional SEM images showed that the samples consisted of columnar nanostructures, with the voids between the columnar grains increasing as the oblique angle was increased owing to the shadowing effect. XRD analysis indicated that crystallite size increased as the oblique angle was increased, although highly oriented thin films were not obtained. The highest mobility and electrical conductivity were observed at an oblique angle of 20° due to the relatively large crystallite size of the thin film obtained at this angle, as well as the small number of voids between the columnar grains. As a result, this film exhibited the highest power factor ($3.1\ \mu W/(cm\cdot K^2)$), approximately six times higher than that obtained by normal sputtering deposition. Therefore, we conclude that using a moderate oblique angle can improve the thermoelectric properties of thin films.

1. Introduction

Recently, there has been growing interest in energy harvesting as a means of providing power to wireless sensor nodes in a widely spread internet of things (IoT) [1,2]. Thermoelectric generators have a number of advantages when harvesting energy from ambient sources, such as direct conversion of energy from heat sources to electricity, or the fact that they are almost maintenance-free due to the absence of moving parts. Wireless sensor nodes do not require thermoelectric generators with high-density electric power, but instead require small, thin generators with low manufacturing costs [3,4]. Thin-film thermoelectric generators are the best candidate to satisfy the requirements of wireless sensor nodes [5–7]. These generators can be miniaturized by employing semiconductor processes or microelectromechanical system (MEMS) processes [8,9]. Moreover, the manufacturing costs of thin-film generators can be reduced because only small amounts of materials are used.

Low-temperature processes are favorable for the fabrication of thin-film thermoelectric generators, as this allows the use of flexible organic substrates such as polyimide [10,11] or polyethylene terephthalate [12,13]. There are several types of film deposition methods with low temperature processes, including sputtering [14,15], plasma enhanced chemical vapor deposition [16,17], and vacuum evaporation [18,19]. Sputtering is the most favorable of these deposition methods, as it obtains relatively high adhesion strengths with the substrate as well as highly uniform thicknesses. To improve the properties of films obtained using the sputtering method, several modifications can be added to the equipment used, such as tilting substrates (oblique deposition) [20,21], applying a DC bias [22,23], and generating hollow cathode plasma [24,25].

One of the most suitable methods for the deposition of thermoelectric thin films is oblique deposition, in which the incident atomic flux impinges the substrate from an oblique angle. This deposition technique is used to manipulate the crystallographic properties of thin films by reducing ion bombardment and facilitating precursor migration on the surface, especially in magnetic [26,27] and optical thin films [28,29]. Thermoelectric properties also depend on the crystallographic properties of the thin films [30,31]. However, to the best of our knowledge, there have been few previous reports presenting thermoelectric thin films fabricated by oblique deposition [32].

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In this study, n-type bismuth telluride (Bi_2Te_3) thin films were prepared using oblique deposition. Bi_2Te_3 was selected as a thermoelectric material since it exhibits good thermoelectric properties around room temperature (RT) [33], which is favorable for energy harvesting applications. The structural and thermoelectric properties of the Bi_2Te_3 thin films were investigated as the oblique angle was changed.

2. Experimental details

N-type Bi_2Te_3 thin films were deposited on a Corning Eagle XG glass substrates (dimensions: 30 mm × 20 mm × 1 mm) using radio-frequency (RF) magnetron sputtering (Tokuda, CFS-8EP). The basic experimental setup has been described in our previous report [34]. A high-purity (99.9%) bismuth telluride target (Chemiston Ltd.) with a diameter of 127 mm and a composition of Bi(32 at.%)-Te(68 at.%) was used. It is to be noted that this atomic composition of the target deviated from the stoichiometric proportion of Bi(40 at.%)-Te(60 at.%). This is because the resulting films' atomic composition, which was measured by using an electron probe microanalyzer (EPMA; EPMA-1610, Shimadzu), was different from that of the target since the sputtering rate of bismuth atoms on the target surface differed from that of tellurium atoms. Therefore, we determined the composition of the target as the resulting films had the atomic composition of Bi(40 at.%)-Te(60 at.%) based on our previous reports [7,35], and assumed that the atomic composition of the thin films did not changed by the oblique angle.

For the oblique deposition, the substrate was tilted in the target in the chamber. The geometric characteristics of the experimental setup are presented in Fig. 1. The substrate was put on a base attached to a substrate holder, and the target-to-substrate distance was fixed at 100 mm. An enclosure was put around the substrate to ensure (as much as possible) that only atoms or ions escaping vertically from the target would reach the substrate. The base allowed the flux angle to be varied, and different values of α (0–80°) were used, where α is the angle between the substrate-to-target direction and the normal of the substrate surface, with an accuracy of ±2% due to the mechanical settings of the substrate holder. Fig. 2 shows pictures of the five types of base ($\alpha = 0°$, 20°, 40°, 60°, and 80°) which were made from acrylonitrile butadiene styrene and fabricated using a 3D printer (da Vinci 1.0 AiO, XYZprinting). Table 1 presents the deposition conditions used for the Bi_2Te_3 thin films. The deposition time was adjusted so that all the samples exhibited a similar film thickness of approximately 1 μm, while other deposition conditions were kept the same throughout all the samples. Prior to film deposition, the chamber was evacuated to a pressure of 2.5×10^{-4} Pa and the substrate temperature was maintained at around RT (30–40 °C). Sputtering was performed in argon gas (99.995%) at a pressure of 1.0 Pa, using an RF power of 200 W, with the deposition time being changed from 10 to 50 min as required.

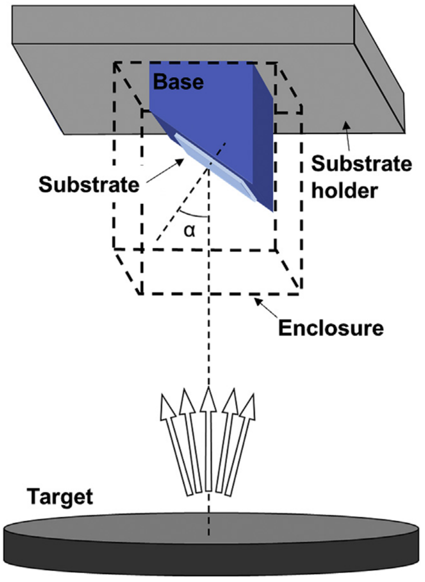

Fig. 1. Schematic diagram of oblique deposition setup.

The cross-sectional morphologies of the Bi_2Te_3 thin films were investigated using scanning electron microscopy (SEM; S-4800, Hitachi) at an electron accelerating voltage of 40 keV. In addition, the film thicknesses were estimated from the cross-sectional SEM images. The atomic compositions of the thin films were estimated by using an electron probe microanalyzer (EPMA; EPMA-1610, Shimadzu). The compositions of the samples were calibrated using the ZAF4 program installed in EPMA-1610. The crystallographic properties of the thin films were evaluated by X-ray diffraction (XRD; Mini Flex II, Rigaku) using Cu-K_α radiation ($\lambda = 0.154$ nm). The average crystallite sizes and crystal orientations of the thin films were determined from the XRD patterns using Rietveld refinement.

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). The mobility, μ, is expressed as $\mu = \sigma/ne$. The in-plane Seebeck coefficient, S, of the thin films was also measured at RT. In order to measure the Seebeck coefficient, both ends of the thin film were connected to a heat sink and a heater. The Seebeck coefficient was determined as the ratio of the potential difference along the film to the temperature difference across it. The in-plane power factor, σS^2, was calculated using the measured electrical conductivity and the Seebeck coefficient.

3. Results and discussion

3.1. Structural properties of Bi_2Te_3 thin films by oblique deposition

Fig. 3 shows the cross-sectional morphologies of five samples of Bi_2Te_3 thin films, as determined using SEM. The normal deposition ($\alpha = 0°$) of a Bi_2Te_3 film resulted in a typical columnar nanostructure with no tilt in the major column axis (Fig. 3(a)). This structure is in agreement with the Thornton's structure-zone model [36], which explains that as-deposited thin films are composed of thin columns at a low substrate temperature. At an oblique angle of 20°, the column axis direction was slightly tilted, at less than 10° from vertical, and no voids between the columnar grains were observed (Fig. 3(b)). The difference between the tilt of the column axis direction and the oblique angle is possibly because the particles collided with each other in the region between the target and the substrate. This increased the distribution of the incident angle of particles, but the particles with higher incident angle (nearly parallel to the substrate) were blocked by the enclosure.

As the oblique angle was increased to 40°, the column axis direction was more tilted compared to that of the thin film created at an oblique angle of 20°, and small voids were observed between the columnar grains (Fig. 3(c)). In addition, columns became shorter, and these short columns were stacked on the substrate. This phenomenon has been observed in previous reports, and is explained by the shadowing effect [37,38]. At an oblique angle of 60°, the number and size of voids increased, as shown in Fig. 3(d). On further increasing the oblique angle to 80° (Fig. 3(d)), the column