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Use of H_2-Ar gas mixtures in radio-frequency magnetron sputtering to produce high-performance nanocrystalline bismuth telluride thin films

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ABSTRACT

Nanocrystalline bismuth telluride (Bi_2Te_3) thin films with good thermoelectric performance were prepared using mixtures of hydrogen and argon gas by radio-frequency magnetron sputtering. The effects of hydrogen addition on the surface morphology, crystal structure, elemental composition, and thermoelectric properties of the Bi_2Te_3 thin films were investigated. The mixing ratio, $H_2/(H_2 + Ar)$, was varied from 0 to 15%. The thin films were deposited on glass substrates heated at 200 °C. It was observed that the surface morphologies of the thin films were greatly affected by the mixing ratio. The deposition rate and composition ratio Te/(Bi + Te) decreased with increasing mixing ratio, indicating that tellurium atoms evaporated from the film surface by a chemical reaction between hydrogen and tellurium. The oxygen concentration inside the films decreased as the mixing ratio increased, resulting in an increased power factor. A maximum power factor of 9.0 μW/(cm·K^2) was observed at a mixing ratio of 10%, as this thin film showed a relatively high electrical conductivity and high Seebeck coefficient. However, at a higher mixing ratio of 15%, the power factor of the thin film drastically decreased, possibly due to the appearance of the hexagonal BiTe phase, which exhibits metallic characteristics. Therefore, we conclude that the addition of a moderate amount of hydrogen (10%) during sputtering can improve the thermoelectric performance of Bi_2Te_3 thin films.

1. Introduction

Thermoelectric materials have been widely used in power generation and Peltier cooling devices as they are able to convert thermal energy into electric energy, and vice versa, convert electricity into heat [1–3]. There are many studies devoted to exploring materials to obtain high thermoelectric performances. Common thermoelectric materials include bismuth telluride (Bi_2Te_3)-based alloys [4–6], lead telluride (PbTe)-based alloys [7,8], and conducting polymers [9–11]. Bi_2Te_3-based materials are the most commonly used thermoelectric materials due to their excellent properties near room temperature (RT), where most applications of power generation and Peltier cooling can be found. The thermoelectric performance is defined by the figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is electrical conductivity, T is the absolute temperature, and κ is thermal conductivity. Therefore, high-performance thermoelectric materials should possess a high power factor $S^2\sigma$ and low thermal conductivity. In addition, Bi_2Te_3 has a rhombohedral crystal structure with quite different lattice constants along each axis (a, b-axis = 0.439 nm and c-axis = 3.148 nm); hence, its exhibits considerable anisotropic behavior [12–14].

To date, power generators and Peltier coolers have been mainly fabricated from bulk Bi_2Te_3-based alloys. However, owing to growing interest in energy harvesting as a means of providing power to wireless sensor nodes in the widely distributed internet of things (IoT) [15,16], thin-film thermoelectric power generators have attracted considerable attention [17–19]. Such thin-film generators can be miniaturized by employing semiconductor processes or microelectromechanical systems (MEMS) [20,21]. Moreover, the manufacturing costs can be reduced as only small amounts of material are required.

Many film fabrication methods, including sputtering [22–24], evaporation [25–27], electrodeposition [28–30], and drop-casting [31–34] have been used to deposit thin films with optimized thermoelectric properties. Magnetron sputtering has attracted remarkable attention as a suitable tool for depositing thin films, as adjusting the sputtering conditions can ensure excellent film quality and adhesion to the substrate [35–38]. To further improve the thermoelectric performance, one approach is to increase the electrical conductivity by adding H_2 gas during sputtering (in general, pure Ar gas atmospheres are used).

It has been reported that the electrical conductivity of transparent conducting oxide (TCO) films, including indium tin oxide (ITO) and doped zinc oxide (ZnO), increased with the introduction of H_2 gas due to an increase in the number of charge carriers in the films [39–42].

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However, to the best of our knowledge, the effects of the use of H_2 gas during sputtering on the structural and thermoelectric properties of thermoelectric thin films have not been extensively investigated. In this study, we aimed to improve the performance of Bi_2Te_3 thin films by investigating the effect of H_2/Ar gas mixtures during sputtering. The structural and thermoelectric properties of the samples were examined while changing the H_2/Ar gas mixing ratio.

2. Material and methods

Bi_2Te_3 thin films were deposited using radio-frequency (RF) magnetron sputtering (CFS-8EP, Tokuda). The basic experimental setup was described in our previous reports [43,44]. Briefly, 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. The atomic composition of the target was determined based on our preliminary study, where we confirmed that the atomic composition of the resulting films with the deposition conditions of only Ar gas had an approximate stoichiometry of Bi(40 at.%)-Te(60 at.%). Glass substrates (Eagle XG, Corning) with dimensions of $20 \times 30\,mm^2$ and 1.1 mm thickness were used. The substrate-to-target distance was set to 140 mm. Prior to film deposition, the chamber was evacuated to a pressure of 2.5×10^{-4} Pa and the substrate temperature was maintained at 200 °C. Sputtering was performed using four different gas mixtures of Ar(100%), Ar(95%)-H_2(5%), Ar(90%)-H_2(10%), and Ar (85%)-H_2(15%), at a pressure of 1.0 Pa and RF power of 200 W. All gases used in the experiments had a purity of 99.995%. The thickness of the deposited films ranged between 0.7 and 1.0 μm, as determined using a super-high vertical resolution non-contact 3D surface profiler (BW-S507, Nikon).

The surface morphologies of the Bi_2Te_3 thin films were investigated using scanning electron microscopy (SEM; S-4800, Hitachi) at an electron accelerating voltage of 3.0 kV. The atomic compositions of bismuth and tellurium were estimated using electron probe microanalysis (EPMA; EPMA-1610, Shimadzu). The compositions of the samples were calibrated using the ZAF4 program supplied with the EPMA-1610 device. The depth profile of the oxygen concentration was estimated using X-ray photoelectron spectroscopy (XPS; PHI Quantera II, ULVAC-PHI). The crystallographic properties of the thin films were evaluated using X-ray diffraction (XRD; Mini Flex II, Rigaku) using Cu-Kα radiation (λ = 0.154 nm). The crystallite size and crystal orientation in the thin films were determined from XRD patterns and Rietveld refinement.

The in-plane Seebeck coefficient, S, of the thin films was measured at RT, where one end of the thin film was connected to a heat sink and the other to a heater. The Seebeck coefficient was determined as the ratio of the potential difference along the film to the temperature difference across it. The electrical conductivity, σ, was also measured at RT using a four-point probe method (RT-70 V, Napson). The in-plane power factor, σS^2, was calculated from the measured Seebeck coefficient and electrical conductivity.

3. Results and discussion

3.1. Structural properties

Here, the Bi_2Te_3 thin film prepared in pure Ar gas will henceforth be referred to as the Bi_2Te_3 thin film with a H_2-Ar mixing ratio, H_2/(H_2 + Ar), of 0%. The surface morphologies of the Bi_2Te_3 thin films with different mixing ratios are shown in Fig. 1. The surface morphology of the thin films was highly dependent on the mixing ratio. The thin film prepared with pure Ar showed a relatively rough surface with densely arranged irregular crystal grains with sharp edges (Fig. 1(a)). With a mixing ratio of 5% (Fig. 1(b)), hexagonal plate-like crystal grains with a plate thickness of ~300 nm and a diameter of ~100 nm were randomly arranged and voids were obvious between the grains. When the mixing ratio was further increased to 10% (Fig. 1(c)), isotropic granular grains with a size of ~100 nm were densely arranged. Increasing the mixing ratio to 15% (Fig. 1(d)) resulted in slightly smaller rounded crystal grains compared to those observed for the mixing ratio of 10%, where the size of the voids between the grains increased slightly. These changes in the surface morphology implied that surface atoms, especially those located at the edges of the grains, evaporated when the proportion of H_2 gas increased.

The deposition rate of the Bi_2Te_3 thin films as a function of H_2/(H_2 + Ar) in the sputtering process is shown in Fig. 2. The deposition rate decreased linearly as the proportion of H_2 gas increased, showing a value of 0.19 nm/s at a mixing ratio of 15%, which was 31% lower than that of the thin films produced in pure Ar. This trend can be explained considering the SEM results and the fact that Bi or Te atoms can be evaporated from the film surface by chemical reaction with the hydrogen atoms. Further, Grochala et al. stated that the enthalpy of formation ΔH_f^o of TeH_2 (99.6 kJ/mol) is lower than that of BiH_3 (217.6 kJ/mol) [45], indicating that TeH_2 is easier to form than BiH_3.

Fig. 3 shows the atomic composition of the thin films with different H_2/(H_2 + Ar) values, as determined by EPMA. The atomic concentration of tellurium and bismuth varied with the mixing ratio. The samples with mixing ratios of 0%, 5%, and 10% showed approximately stoichiometric proportions. However, when the mixing ratio increased to 15%, the concentration of bismuth increased, while that of tellurium decreased. Hence, the atomic composition was Bi:56 at.% and Te:44 at.%, which significantly deviated from the stoichiometric proportion (Bi:40 at.% and Te:60 at.%). Considering both the deposition rate and atomic composition, we conclude that Te atoms were mainly evaporated from the film surface by chemical reaction with hydrogen, producing hydrogen telluride [46,47].

Hydrogen is known to behave as a reducing agent; hence, we investigated the depth profile of the oxygen concentration inside Bi_2Te_3 thin films using XPS, as shown in Fig. 4. Note that all samples exhibited higher oxygen concentrations near the film surface due to surface oxidation and adsorption of moisture. The oxygen concentration in the thin film at a mixing ratio of 0% was clearly higher than those of films prepared with H_2-Ar mixtures. However, the oxygen concentration in all samples varied in the depth direction. Therefore, we estimated the average oxygen concentration in the depth profile (d > 200 nm), and these values are shown in the inset of this figure. The average oxygen concentration inside the thin films greatly decreased when H_2 gas was used in the sputtering process. The average oxygen concentration inside the thin films at a mixing ratio of 5% was 0.34 at.%, while that of the sample prepared with pure Ar was 0.82 at.%. When the mixing ratio was further increased, the averaged oxygen concentration of the thin films at mixing ratios of 10% and 15% decreased to approximately 0.15 at.%. Therefore, we conclude that using H_2-Ar mixtures in the sputtering process contributed to a decrease in the oxygen concentration inside the Bi_2Te_3 thin films.

XRD patterns of the Bi_2Te_3 thin films with different H_2-Ar gas mixing ratios are shown in Fig. 5. The three samples at the mixing ratios of 0%, 5%, and 10% exhibited peaks corresponding to the rhombohedral phase of Bi_2Te_3 (JCPDS 15-0863). The XRD peaks corresponding to the c-axis-oriented peaks of (0 0 l) and (0 1 5) were predominantly observed in the three samples. The highest XRD peak was (0 0 6) at the mixing ratios of 0% and 5%, but changed to (0 1 5) at a mixing ratio of 10%. This indicates that the crystal orientation in the thin films was dependent on the proportion of H_2 gas. However, the thin film produced at a mixing ratio of 15% showed two crystal phases, the rhombohedral phase of Bi_2Te_3 (JCPDS 15-0863) and the hexagonal phase of BiTe (JCPDS 31-0200). This was likely due to the evaporation of Te atoms from the thin film. Thus, we consider that an excessive amount of H_2 gas in the sputtering process yielded other crystal phases, such as the BiTe phase. Similar behavior was observed for this material in a high-temperature thermal annealing process [48,49].

To further investigate the crystal structures of the Bi_2Te_3 thin films,

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