Journal of Alloys and Compounds 773 (2019) 78–85

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Simultaneous stoichiometric composition and highly (00*l*) orientation of flexible Bi_2Te_3thin films via optimising the DC magnetron sputter-deposition process

Nuttakrit Somdock [a], Supasak Kianwimol [a], Adul Harnwunggmoung [b], Aparporn Sakulkalavek [a], Rachsak Sakdanuphab [c, *]

[a] Department of Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Rd. Ladkrabang, Bangkok, 10520, Thailand
[b] Faculty of Science and Technology, Rajamangala University of Technology, Suvarnabhumi, Nonthaburi, 11000, Thailand
[c] College of Advanced Manufacturing Innovation, King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Rd. Ladkrabang, Bangkok, 10520, Thailand

A R T I C L E I N F O

Article history:
Received 17 April 2018
Received in revised form
4 September 2018
Accepted 17 September 2018
Available online 20 September 2018

Keywords:
Flexible bismuth telluride
(00*l*) orientation
DC sputtering

A B S T R A C T

Simultaneous stoichiometric composition and highly (00*l*) orientation of flexible Bi_2Te_3 thin films were investigated under the DC magnetron sputtering parameters. Stoichiometric Bi_2Te_3 and highly (00*l*) orientation structure was obtained by sputtering conditions, preheat temperature at 350 °C, and working pressure of 1.8×10^{-3} mbar. This designed structure of layered compact feature with stoichiometry provide the relatively high mobility. The maximum carrier mobility of 118 cm^2/V was observed for highly (00*l*) film. The electrical conductivity of thin film has been greatly enhanced, to a maximum of about 14.90×10^3 S/cm at 50 °C. This value is higher than those of hot-pressed or spark plasma sintering n-type Bi_2Te_3 bulk alloys. The maximum power factor of 12.5×10^{-3} W/m.K^2 was obtained at 300 °C.

1. Introduction

Thermoelectric (TE) materials can convert heat into electricity directly and reversibly through Seebeck and Peltier effects, respectively. The TE devices have promising applications in power generation and cooling [1–4]. The performance of thermoelectric materials is driven by the figure of merit $ZT = S^2\sigma T/K$, where S, σ, K, and T are the Seebeck coefficient (V/K), electrical conductivity (S/m), thermal conductivity (W/mK), and the absolute temperature (K), respectively. To enhance thermoelectric performance, the low-dimension thermoelectric materials have been promised due to the recent demonstration of high power factor (*PF*) $S^2\sigma$ and low thermal conductivity (K) [4]. Thermoelectric thin film is one of the important low-dimensional thermoelectric materials that have been investigated in order to achieve less thermal conductivity (K) and increasing the ZT value [5–7].

Bismuth telluride compound is known to be the best thermoelectric material at room temperature [8,9]. Because the bismuth telluride material is an anisotropic material, the properties of this material depend on the structure and different orientation plane of thin film. Therefore, the thermoelectric properties along the *a*-axis are superior to those along the *c*-axis. According to previous studies, it expected that orientation of (00*l*) plane in bismuth telluride thin film will increase the thermoelectric properties [10–13]. For bismuth telluride thin films with a highly (00*l*) orientation plane, the *PF* values were about 18.2–38.0 μWcm^{-1} K^{-2} [10–12] while the *PF* of bismuth telluride thin films with a highly (015) orientation plane with the *PF* values were about 4 – 8μWcm^{-1} K^{-2} [11,14–16]. Another factor was the chemical composition: bismuth telluride thin films required a stoichiometric ration of [Bi] and [Te] for achieving the best thermoelectric performance.

There are many techniques of preparing the bismuth telluride thin films with highly (00*l*) orientation plane and enhanced thermoelectric properties, such as metal organic chemical vapour phase deposition (MOCVD) [17,18], pulsed laser deposition (PLD) [12,13], molecular beam epitaxy (MBE) [19,20], and sputtering [10,11,22]. The MOCVD, PLD, and MBE equipment are expensive but are good control in the film composition. However, the sputtering technique is a good candidate due to its inexpensive equipment, high deposition rate, good reproducibility, and possibility for scaling to

* Corresponding author.
E-mail address: rachsak.sa@kmitl.ac.th (R. Sakdanuphab).

https://doi.org/10.1016/j.jallcom.2018.09.216
0925-8388/

commercial [23,24]. In the bismuth telluride sputtering process, the substrate temperature was an important factor. The temperature range of 220–380 °C was suitable for the film deposition because it can create the lowest surface energy of the substrate [12]. The results of the lowest surface energy of the substrate prefer (00*l*) orientation layers [12,13]. However, the temperature affected to the chemical composition, due to the re-evaporation of Te at high temperature. The non-stoichiometric bismuth telluride films were obtained with the low thermoelectric performance. For the composition control of bismuth telluride in a co-sputtering technique, the sputtering power was adjusted on Bi and Te targets [8,25]. For example, Deng et al. [11] have reported special depositing condition to produce *c*-axis oriented Bi_2Te_3 thin films by co-sputtering method. However, Bi_2Te_3 and additional Te targets were required to obtain the stoichiometric composition. Only a few works studied the control of [Bi] and [Te] ratio from a Bi_2Te_3 target [21]. Nuthongkum et al. deposited bismuth telluride on flexible substrate using Bi_2Te_3 target by RF magnetron sputtering and reported that the working pressure was significant for controlling composition and improving thermoelectric properties of Bi-Te thin films [21]. However, it is further study of the control both stoichiometric composition and highly *(00l)* orientation of bismuth telluride thin film.

In this paper, the flexible bismuth telluride thin films were deposited by DC magnetron sputtering using the Bi_2Te_3 target. We suggest a simple deposition condition to control both the chemical composition and preferential growth of different crystal planes. Simultaneous stoichiometric composition and highly *(00l)* orientation of flexible Bi_2Te_3 thin films were investigated under the DC magnetron sputtering parameters.

2. Experimental

2.1. Bismuth telluride thin film deposition

Bismuth telluride thin films were deposited on polyimide-film substrates (DuPont™Kapton®) with a dimension of $2.5 \times 7.5\ cm^2$ using the DC magnetron sputtering technique. The polyimide film substrates were (1) attached to a glass slide; (2) cleaned in ultrasonic bath with methanol, acetone, and deionized water for 10 min; and then (3) dried the substrate by nitrogen gas. For the sputtering system, a 3-in diameter of Bi_2Te_3 target (high purity: 99.9%) was used and the distance between the target and substrate was 50 mm. Before the deposition process, the base pressure of the deposition chamber was below 2.5×10^{-5} mbar and pre-sputtering was employed for 5 min. The halogen lamp heater was used to preheat the substrate at 350 °C for 15 min and then was turned off during the deposition. Bismuth telluride thin films were immediately deposited at the DC power of 45 W for 5 min while working pressure was varied from 1.4×10^{-2},1.6×10^{-2}, 1.8×10^{-2}, and 2.0×10^{-2} mbar.

2.2. Thin film measurements and characterisation

The surface morphology and cross-section of the bismuth telluride thin films were investigated by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F). The bismuth telluride films were analysed by X-ray photoelectron spectroscopy (XPS, Kratos, Axis ultra DLD). The orientation and the crystalline structure of bismuth telluride thin films were investigated by X-ray diffraction (XRD, PANalytical EMPYREAN) with CuKα radiation (λ = 1.5405980) in the range 2θ from 10 to 80° and transmission electron microscopy (TEM, JEOL JEM-2100). The carrier concentration and Hall mobility at room temperature of the thin films were measured using the four-probe method with the Hall Effect measurement (ECOPIA HMS3000). The electrical conductivity and the Seebeck coefficient were measured with a ZEM-3 (ULVAC-Riko) at 25–300 °C. The uncertainty of the Seebeck coefficient and electrical conductivity measurement is 3% [26].

3. Results and discussion

Fig. 1 shows the XPS spectra of the bismuth telluride thin films. The surface chemical composition was determined by the decomposition of XPS peaks at Te $3d_{5/2}$, Te $3d_{3/2}$ and Bi $4f_{7/2}$, Bi $4f_{5/2}$ binding energy, using least-squares curves fitting. The atomic ratio of Bi and Te were calculated and shown in Table 1. The Te content increases as the working pressure increases from 1.4×10^{-2} to 1.8×10^{-2} mbar. The nearly stoichiometric bismuth telluride thin films were achieved at Te content 60.98 at.%. However, the working pressure was up to 2.0×10^{-2} mbar, the Te content was slightly decreased. The results of the Te content increased from 55.46 at.% to 60.98 at.% due to the density of the sputtering gas in the deposition system will also increase the collision probability between sputtered particles. Typically, the atomic mass of the Bi element is larger than Te (Bi = 143pm and Te = 123pm) [5]. Thus, the Bi elements were obstructed by the Ar gas increase, thereby affecting the composition and films composition. However, the Te content of the thin film decreased to 58.18 at.% with deposited at the working pressure 2.0×10^{-2} mbar. The decrease of Te content may be because both Bi and Te elements were obstructed when Ar gas pressure is relatively high [21]. This result is consistent with our

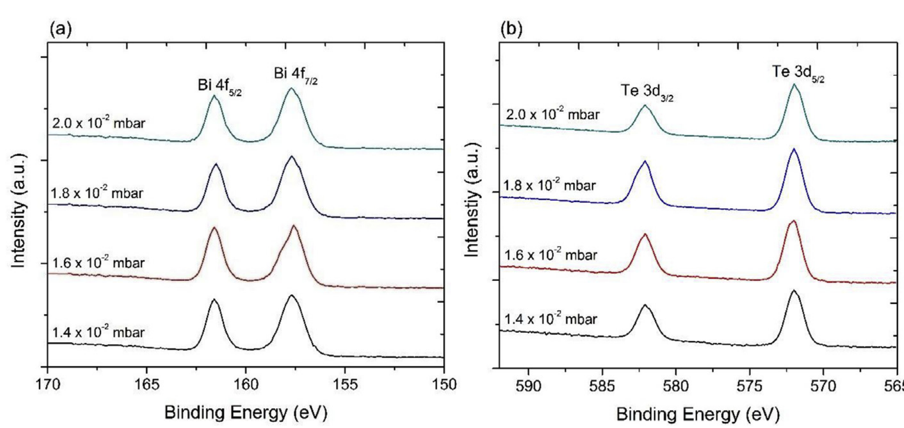

Fig. 1. XPS spectrum of bismuth telluride thin films at different working pressure.