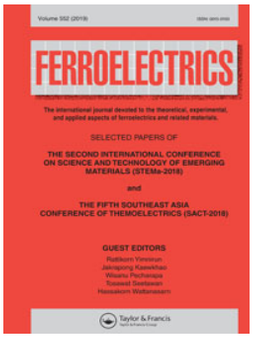

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Comparison of thermoelectric properties of flexible bismuth telluride thin films deposited via DC and RF magnetron sputtering

Piya Jitthamapirom[a], Pornsiri Wanarattikan[b], Pilaipon Nuthongkum[c], Rachsak Sakdanuphab[a], and Aparporn Sakulkalavek[c]

[a]College of Advanced Manufacturing Innovation, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand; [b]Division of Physical Science, Faculty of Science and Technology, Huachiew Chalermprakiet University, Samut Prakan, Thailand; [c]Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand

ABSTRACT

Bi_2Te_3 thin films were deposited onto polyamide sheets with direct current (DC) or radio frequency (RF) magnetron sputtering techniques. The films were prepared using a Bi_2Te_3 target at a varying pre-heating temperature from 150 to 350 °C. It was observed that the type of plasma excitation and pre-heating temperature can significantly change the composition, preferred orientation, crystallinity, and thermoelectric properties of the films. The pre-heat treatment significantly affected the non-stoichiometric composition. In addition, it was shown that crystallinity and (0 0 *l*) planes were enhanced in the DC sputtered coatings at a high pre-heating temperature. The maximum power factor of 3.5×10^{-3} W/m K^2 at 285 °C was obtained for the films deposited using DC magnetron sputtering and a pre-heating temperature of 350 °C. The carrier concentration and mobility of the film were 5.40×10^{20} cm^{-3} and 13.04 cm^2/V s, respectively. Compared with an ordinary Bi_2Te_3 film, the power factor of such film has been greatly increased. The results indicated that DC magnetron sputtering can enhance the (0 0*l*) plane orientation in the Bi_2Te_3 film.

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KEYWORDS
Flexible Bi_2Te_3; DC/RF magnetron sputtering; (0 0 *l*) preferred orientation

1. Introduction

Bismuth telluride material has high thermoelectric efficiency that has been used for the thermoelectric generators (TEGs) and thermoelectric coolers (TECs). This good material has high dimensionless figure of merit (*ZT*) defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity, and T is the absolute temperature. The ZT value is thermoelectric conversion efficiency of thermoelectric materials. The ZT value can be improved using a low-dimensional structure to increase the power factor and/or decrease the thermal conductivity [1, 2]. The low-dimensional thermoelectric materials such as thin films and nanostructures could increase the PF and the ZT because of its stronger quantum confinement geometries than that of their

CONTACT Aparporn Sakulkalavek aparporn.sa@kmitl.ac.th
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bulk. Several techniques have been investigated for the deposition of Bi_2Te_3 thin films [3–7], that is, pulsed laser deposition, co-evaporation, and magnetron sputtering [1, 2, 5–7]. Among the deposition techniques used for Bi_2Te_3 fabrication, magnetron sputtering is widely employed because of its flexibility in controlling the composition and microstructure. The development of the deposition process for depositing Bi_2Te_3 films has been investigated [2–7]. Co-sputtering is required for the stoichiometry of Bi_2Te_3. In addition, the annealing temperature is needed to enhance the thermoelectric properties of the film by reducing defects and improving the crystallinity. Moreover, the loss of the Te content with the increase of annealing temperature due to the re-evaporation of volatile Te elements is concerned. However, the problem to control the stoichiometric Bi_2Te_3 composition of [Bi]:[Te] = 2:3 is very important. From our previous work, the stoichiometry of Bi_2Te_3 and Sb_2Te_3 thin films has been obtained by adjusting sputtering parameters, that is, working pressure and pre-heating substrate temperature [1, 2, 8]. Pre-heating treatment is used to sufficiently increase the initial substrate temperature to gain the Te fusion and accumulate in the plasma. Then the accumulated Te are re-deposited on the substrate during the temperature gradually decreases [1].

Most of the previous studies used RF magnetron sputtering during the deposition process [2, 5, 7]. However, a Bi_2Te_3 target has a resistivity of less than $10^{-3}\,\Omega\,cm$, which is available for both RF and DC magnetron sputtering. In addition, RF magnetron sputtering is a complex system that needs a separate impedance matching network as an additional component. DC magnetron sputtering is significantly more cost effective, and it is the most widely industrially used technique [9]. Comparison of the thermoelectric properties of flexible Bi_2Te_3 deposited by DC or RF magnetron sputtering have been studied for the first time. The combined effects of the pre-heating temperature and type of plasma excitation (DC and RF supply) on the crystal structure, chemical composition, electrical, and thermoelectrical properties of bismuth telluride were studied.

2. Experimental details

Polyimide sheets (DuPont^{TM}Kapton$^{®}$) were used as a flexible substrate for the deposition of Bi_2Te_3 thin films with DC or RF magnetron sputtering. Alloy Bi_2Te_3 target with purity of 99.9% from Stanford Advanced Materials was used in the sputtering process. Polyimide sheet is the best flexible substrates because of its good mechanical, physical, and electrical properties in widely temperature range [2]. The substrate to target distance was 50 mm. The substrate was ultrasonic cleaned with deionized water and ethanol, following blown dry with nitrogen gas. The rotary and diffusion pumps were used to evacuate the sputtering system to a base pressure of 6.0×10^{-6} mbar and flushed with argon gases several times. Before the deposition, the Bi_2Te_3 target was pre-sputtered under the Ar gas for 5 min to remove contamination on its target surface. The DC and RF sputtering power was constant (45 W), and the sputtering pressure of 1.3×10^{-2} mbar was used. Film thickness of 0.5 µm was controlled in both DC and RF magnetron sputtering *via* the deposition time while pre-heating temperature was varied between 150 and 350 °C. The microstructural properties and chemical composition of the films were studied by means of grazing incidence X-ray diffraction (BRUKER AXS D8 DISCOVER XRD) and field emission scanning electron microscopy with energy

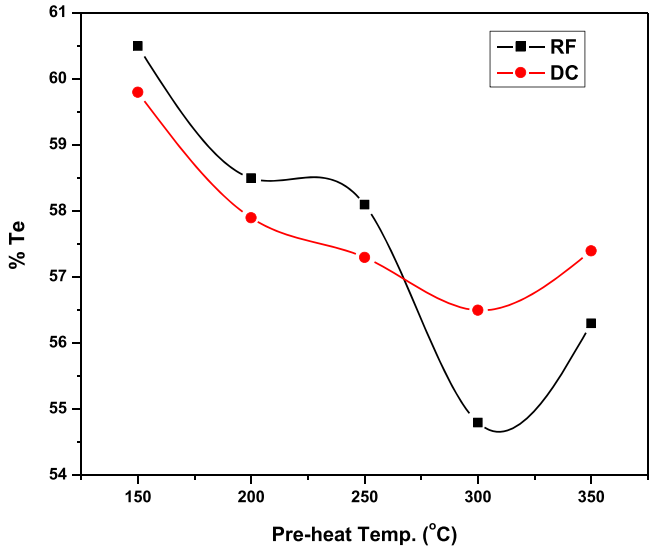

Figure 1. Te content in the Bi–Te thin film deposited using DC and RF magnetron sputtering at different preheating temperatures.

dispersive X-ray spectroscopy (JEOL, JSM-7001F with Oxford Instruments, X-Max^N 20 SSD), respectively. The electrical properties were carried out by using Hall measurements (Ecopia, HMS3000) for Hall mobility and carrier concentration. The temperature-dependent Seebeck coefficient (S) and electrical conductivity (σ) were obtained at 50–300 °C by the DC four-terminal method (ULVAC-RIKO, ZEM-3).

3. Results and discussion

Energy-dispersive X-ray spectroscopy (EDS) provides chemical composition of the deposited Bi-Te films, as shown in Figure 1. It can be seen that both DC and RF magnetron sputtering exhibit a similar behavior of decreasing %Te with increasing pre-heating temperature. The Te content decreased with increasing pre-heating temperature up to 300 °C and increased with increasing pre-heating temperature at 350 °C. This is considered to result from the Te atom evaporation at the temperature up to 300 °C, which caused the concentration of %Te to decrease. However, at the higher temperature range of 300–350 °C, the %Te values clearly increase when the preheat substrate temperature rises from 300 to 350 °C. It can be described by the re-deposition of Te accumulated in the plasma during high substrate temperature, as explained in our previous work [1]. While the substrate temperature is cooling down, the Te atoms in plasma are redeposited on the substrate.

Figure 2 presents the XRD spectra of the DC and RF sputtering Bi–Te thin films with pre-heating temperatures at 150 and 350 °C. The XRD peaks were indexed to (0 0 6), (0 1 5), and (0 0 1 5) of Bi_2Te_3 structure (JCPDS card 72-2036). In addition, the intensity of diffraction peaks is stronger at the elevated pre-heating temperature, and the crystallinity of Bi–Te films is improved. The thermal diffusion of atoms reduces the dislocated atomic occupancies and enhances the coalescence of adjacent grains, which leads to the improved crystallinity of the films. It is interesting to note that the films

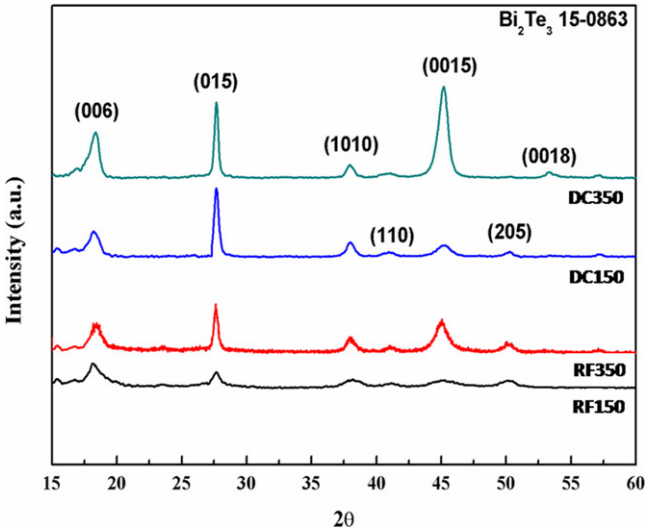

Figure 2. XRD spectra of Bi–Te thin films with a different type of plasma excitation and pre-heating temperature.

with a pre-heating temperature at 350 °C (DC350 and RF350) show an increase in preferred orientation of (0 0 6) and (0 0 1 5) planes, as seen in Figure 2. This result is consistent with the works of Shang *et al.* [10] and Zhang *et al.* [11] who indicated the requirement of increased substrate temperature to enhance the orientation of the (0 0 *l*) planes.

Jiang *et al.* [12] calculated surface energy of Bi_2Te_3 *via* the first-principles density functional theory using the Vienna *ab initio* simulation package (VASP). The calculated surface energies were 0.16, 0.37, and 0.63 J/m^2, for (0 0 1), (0 1 5), and (1 0 0), respectively. This result indicates that (0 0 *l*) is the lowest energy surface. Hence, the (0 0 *l*) surface is expected to be the preferred orientation at elevated growth temperatures, where adatom mobilities are sufficient to form crystallites bounded by low energy planes during nucleation [13]. In this study, the different orientation of Bi–Te thin films can be contributed using DC or RF magnetron sputtering techniques under the pre-heating temperature.

The difference between DC and RF magnetron sputtering affects ion bombardment on the sputtering target and electron accumulation on its substrate and target. DC sputtering directly transfers kinetic energy to sputtered atoms, and the mobility of adatoms is higher than that during the RF sputtering at the same sputtering power [14]. The increase of sputtered atom energy is a factor that enhances (0 0 *l*). Another factor is that deposited atoms obtain more energy to form (0 0 *l*) crystal orientation at the high pre-heating temperature.

Table 1 shows the XRD analysis of Bi–Te thin films. The grain size (D) was calculated based on the Scherrer's Eq. (1),

$$D = k\lambda/\beta\cos\theta \tag{1}$$

where $k = 0.94$, λ is wavelength of X-ray radiation, β is peak full width at half maximum (FWHM), and θ is the Bragg angle. The intensity ratio of the sum of all of the

Table 1. X-ray diffraction analysis of Bi–Te thin films with different deposition conditions.

		Grain size (nm)	
Films	$\sum(0\ 0\ l)\ /\sum(h\ k\ l)$	(0 1 5)	(0 0 1 5)
RF150	0.38	11.5	N/A
RF350	0.43	19.7	12.1
DC150	0.39	24.9	N/A
DC350	0.60	27.6	24.5

c-axis oriented peaks, $\sum\{0\,0\,l\}$, to the sum of all the peaks, $\sum\{h\,k\,l\}$, were estimated from 0.38 to 0.60. The highly $(0\,0\,l)$ oriented Bi_2Te_3 thin films have been successfully deposited using the DC magnetron co-sputtering method with post annealing at 350 °C [11].

Table 2 shows the carrier density, carrier mobility, and electrical conductivity at room temperature of the films. The carrier density is determined by the Te content (%Te) that corresponds to defects in the films. The carrier density decreases from 5.70×10^{20} to $4.16 \times 10^{20}\,cm^{-3}$ with the %Te increase from 56.3 to 60.5. Thus, the increase of carrier density may be ascribed to the deviations from the stoichiometric composition. The non-stoichiometric films enhance the carrier density of the films [1]. The carrier mobility of the films is 3.17–13.04 $cm^2/V\,s$ and correspond to the increase of grain sizes and $(0\,0\,l)$ orientation. It is surprising that the carrier mobility of more than 10 $cm^2/V\,s$ was obtained using only the DC sputtering technique and pre-heating treatment. The film deposited *via* RF magnetron sputtering exhibited lower carrier mobility than that deposited *via* DC magnetron sputtering. In addition, the mobility of the DC350 thin film was similar to Deng *et al.* (12.1 $cm^2/V\,s$) [15], who deposited bismuth telluride film using the substrate temperature of 350 °C. In general, the large crystallite sizes lead to increase the carrier mean free path due to the reduction in grain boundary scattering. In addition, the $(0\,0\,l)$ preferred orientation has been shown benefit to increase the carrier mobility along the *ab*-plane. Electrical conductivity is determined *via* carrier concentration and mobility, as described using the following relationship:

$$\sigma = ne\mu \tag{2}$$

where n is the carrier density, μ is the carrier mobility, and e is the electronic charge. The carrier mobility plays an important role in the electrical conductivity of the Bi–Te thin films. The increase of electrical conductivity from 2.12×10^2 to 11.27×10^2 S/cm is related to the increase of carrier mobility. However, the carrier density slightly affects the electrical conductivity. In addition, the electrical conductivity of the films deposited using DC sputtering is much higher (approximately three-times higher) than using RF sputtering. The increase in electrical conductivity was due to the enhanced crystal size and $(0\,0\,l)$ texture in the films. The electrical conductivity of the DC350 thin film is comparable with those of hot-pressed or SPS sintered n-type Bi_2Te_3-based bulk alloys [16, 17].

Subsequently, temperature-dependent electrical conductivity, $\sigma(T)$, of the Bi–Te films was determined for the in-plane electrical transport properties, as shown in Figure 3. The result shows that σ of the film deposited *via* DC sputtering is higher than the film deposited *via* RF sputtering over the entire temperature range. The σ of all film increased with increasing temperature from 50 to 200 °C, indicating a typical

Table 2. Expression of the electrical properties of the Bi–Te thin films with the %Te.

Films	%Te	Carrier density ($\times 10^{20}$ cm^{-3})	Carrier mobility (cm^2/V s)	Electrical conductivity ($\times 10^2$ S/cm)
RF150	60.5	4.16	3.17	2.12
RF350	56.3	5.70	5.06	4.61
DC150	59.8	4.51	8.39	6.06
DC350	57.4	5.40	13.04	11.27

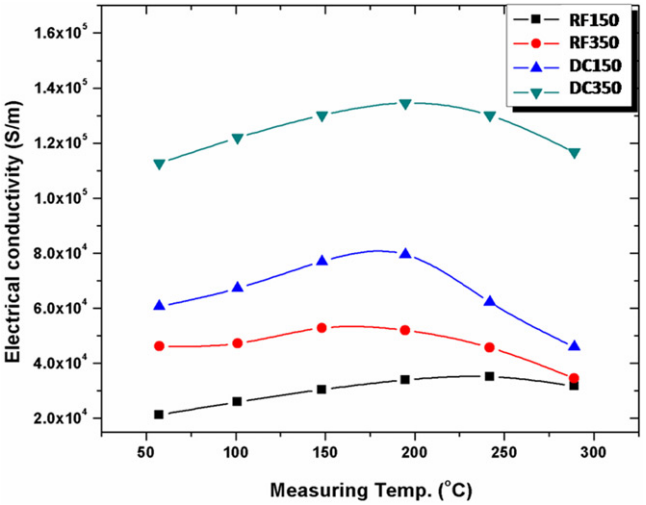

Figure 3. Electrical conductivity of Bi–Te films as a function of temperature.

semiconductor-like behavior. In contrast, for the temperature above 200 °C, the σ values gradually decreased with increasing temperature. This is probably due to the increase of carrier scattering with the carrier density increase. In this work, the DC350 film has the maximum electrical conductivity of 1.4×10^5 S/m at a measurement temperature of 200 °C.

Figure 4 shows the temperature-dependent Seebeck coefficient (S) of the Bi–Te thin films measured from 50 to 285 °C. The S values of the films exhibit negative value, indicating the majority carriers of electrons for n-type semiconductor. It can be seen that all of the films exhibit a similar behavior of temperature dependent Seebeck coefficient. S value increases with increasing temperature, that usually be explained by the behavior of heavily doped degenerate semiconductor regimes. The maximum Seebeck coefficient is observed on the DC350 film, and the Seebeck coefficients are in the range of 90–180 μV/K.

The in-plane temperature-dependent power factors ($S^2\sigma$) of Bi–Te films are shown in Figure 5. The power factor values of both DC and RF films increase with increasing temperature. This was due to the increase of electrical conductivity and Seebeck coefficient with the temperature increase. The maximum power factor of 3.5×10^{-3} W/m K^2 at 285 °C was obtained for the DC350 film. In comparison with the previous works by Kim *et al.* [6, 18], Huang *et al.* [7], and Bourgault *et al.* [19] [power factor was below 1.2×10^{-3} W/(m K^2)], our results show the highest power factor. The films deposited using DC magnetron sputtering exhibit better thermoelectric performance than those deposited using RF magnetron sputtering. Generally, the stoichiometric Bi_2Te_3 film has

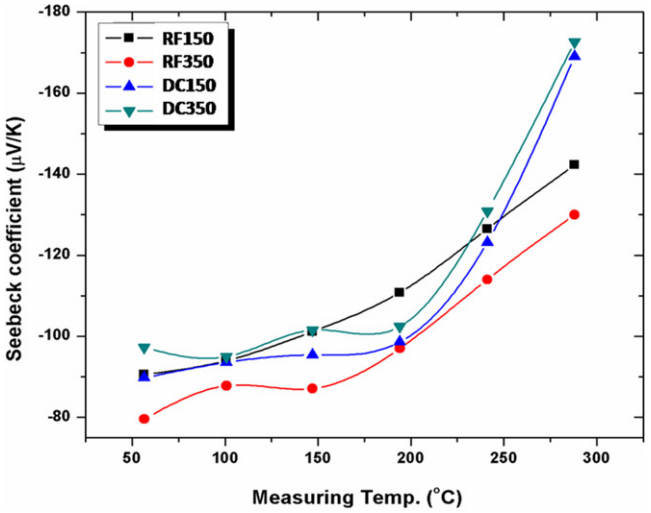

Figure 4. Seebeck coefficient of the Bi–Te films as a function of temperature.

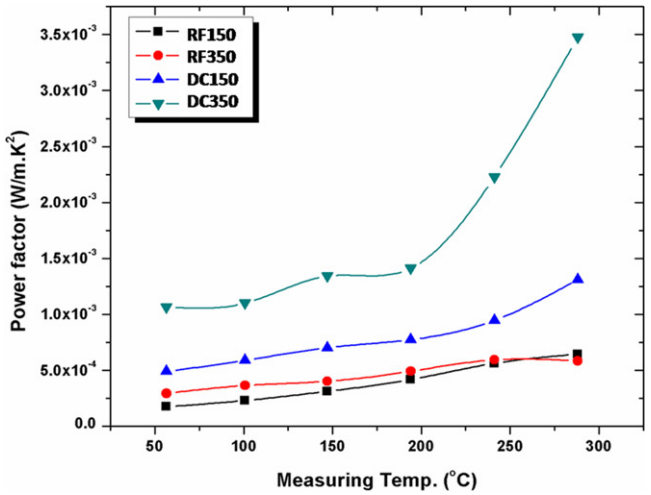

Figure 5. Power factor of the Bi–Te films as a function of measuring temperature.

good thermoelectric properties. Although, the RF150 and DC150 films have a nearly stoichiometric composition, the power factor of the films is less than 1.25×10^{-3} W/m K^2 in the temperature range of 50–285 °C. Therefore, the stoichiometric composition and the (0 0 *l*)-preferred orientation of the films are required for the best thermoelectric application. From our results, the DC magnetron sputtering process is the candidate for obtaining highly (0 0 *l*) oriented Bi_2Te_3 films with a stoichiometric composition, which may also be favorable for the improvement of thermoelectric properties.

4. Conclusion

In summary, DC and RF magnetron sputtering Bi–Te thin films with different pre-heating temperatures were investigated and compared. The energy of sputtered atoms using

different ion bombardment and substrate temperatures were the key parameters for controlling the crystal quality and orientation. The increase of grain size and (0 0 *l*)-oriented Bi_2Te_3 films were also favorable for the improvement of thermoelectric properties. The best thermoelectric performance of the Bi_2Te_3 film was achieved using the DC magnetron sputtering deposition with a pre-heating temperature of 350 °C. Consequently, the power factor of 3.5×10^{-3} W/(m K^2) at 285 °C was obtained. However, the DC magnetron sputtering with a pre-heating temperature of 350 °C resulted in films with a non-stoichiometric composition. Further studies of the DC magnetron sputtering process are necessary to achieve both the highly (0 0 *l*) oriented Bi_2Te_3 films and the stoichiometric composition.

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