Effect of Microwave-assisted Post-treatment on the Structural, Electrical, and Thermoelectric Properties of Flexible Sb_2Te_3 Films Prepared by DC Magnetron Sputtering

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Abstract

Flexible Antimony telluride (Sb_2Te_3) thin films were coated on a polyimide substrate by DC magnetron sputtering using an alloy 99.9% Sb_2Te_3 target. The effects of microwave-assisted post-treatment at various temperatures 473, 523, 573, and 623 K for 1 min under N_2 atmosphere on the [Sb]:[Te] ratio, structural, surface morphology, electrical, and thermoelectric properties were studied. The [Sb]:[Te] ratio of flexible Sb_2Te_3 film was determined by energy dispersive spectrometry (EDS). EDS analysis revealed that the Te ratio was slightly decreased when heat treatment increased. The crystal structure and surface morphology of flexible films were characterized by x-ray diffraction (XRD) and a field emission scanning electron microscope (FE-SEM), respectively. All samples confirmed the polycrystalline Sb_2Te_3 with a hexagonal structure. The crystallinity is heightened by the heat treatment process. Electrical transport properties were measured by Hall Effect measurements. The Seebeck coefficient and electrical conductivity were simultaneously measured at room temperature by a DC four-terminal method (Seebeck Coefficient/Electrical Resistance Measurement System). The results indicated that the microwave heat treatment can enhance the electrical conductivity and Seebeck coefficient of the flexible films leading to reaching a maximum power factor of 1.71 mW/K^{2}m, which is annealed at 523 K.

Keywords: Flexible Sb_2Te_3, Microwave heating, Post-treatment, DC magnetron sputtering

1. Introduction

Antimony telluride (Sb_2Te_3) is included in a class of thermoelectric (TE) semiconductors, based on a general formula $A_2^V B_3^{VI}$ with a narrow band gap (0.26 eV). Sb_2Te_3 compounds have a rhombohedral crystal structure with five atoms per unit cell belonging to the space group $R\bar{3}m$. These materials can be converted from thermal to electrical energy through the Seebeck effect and electrical to thermal energy through the Peltier effect. The efficiency of conversion of TE is expressed by the thermoelectric figure of merit $ZT=S^2\sigma T/\kappa$ where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the total thermal conductivity. A high ZT is achieved when enhancing the power factor according to the equation $PF = S^2\sigma$ and reducing total thermal conductivity. Typically, the excellent ZT of Sb_2Te_3 has achieved near room temperature at 300 K [1]-[2] which corresponds to a low-temperature heat source (300-400 K). For integrated devices into the heat sources, polyimide flexible substrates are attractive due to their ability to withstand a wide range of temperatures (4-673 K), electrical and chemical resistance, and suitable value of thermal expansion coefficient which matches with telluride films. Various techniques such as evaporation [3],

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co-evaporation [4], electrochemical deposition [5], pulse laser deposition [6], and sputtering [7] have been employed to deposit Sb_2Te_3 films. The magnetron sputtering technique is commonly used as it offers high purity of film and excellent uniformity on large-area deposition. Moreover, sputtering parameters such as sputtering power, target source, working pressure, deposition rate, gas flow, and temperature can be controlled during the sputtering process to achieve an excellent-quality film [8], [9].

To the best of our knowledge, high-performance Sb_2Te_3 films were always deposited and followed by a thermal treatment step after the deposition process to improve the inter-particle, film adhesion, crystallinity, porosity, and conductivity of the films leading to enhance structural, electrical, and thermoelectric properties [7], [13]. In many previous works [7]-[13], a long reaction time of thermal treatment has produced the evaporation of Te elements and leads to the correlation of non-stoichiometric composition [7]. The short reaction time during thermal treatment was designed to prevent the evaporation of Te elements [8], [13]. Microwave post-treatment is interesting as an innovative technology as it has various advantages to focus attention on this technology over conventional annealing methods including rapid thermal treatment development, reduced processing temperature, better production quality, uniformly, less expensively controllable and energy saving [14]. Moreover, the unique internal heating of microwave energy can lead to overcoming the non-uniform heat distribution of the conventional method [12], [13], [15].

In this study, P-type Sb_2Te_3 flexible films were deposited by DC magnetron sputtering and rapid heat treatment using a microwave for a short duration time for 1 min was employed to enhance their properties. The influence of microwave-assisted post-treatment on the structural, electrical, and thermoelectric properties of sputtered Sb_2Te_3 flexible films was investigated.

2. Experimental

2.1 Experimental setup

Flexible polyimide substrates of 0.025 mm thickness (DuPont Kapton) were cut to 25 mm × 75 mm and attached to a glass slide. they were cleaned via a series of 10 min ultrasonic methanol and de-ionized water and finally dried with N_2 gas. Sb_2Te_3 films were deposited on the flexible substrates by direct current magnetron sputtering technique using high purity Sb_2Te_3 alloy target (purity: 99.9% with a diameter of 3 inches, Stanford Advanced Materials). High-purity Ar gas was introduced through a mass flow controller after the vacuum chamber had been evacuated below 2.7×10^{-5} mbar using a diffusion pump backed by a rotary vane pump before deposition [13]. The sputtering power was 35 W and the working pressure was maintained at 2.6×10^{-2} mbar. A 10 min pre-sputtering was performed on the target surface to remove native oxide and contamination. The pre-heat temperature was employed at 673 K for 15 min before deposition. The sputtering time was fixed for 6 min. Finally, the sputtered Sb_2Te_3 films on flexible polyimide were obtained. Microwave-assisted thermal treatment was performed using a microwave (Samsung 0M75S) operating at 2.45 GHz with a power of 800W. The samples were heated treatment at 473, 523, 573, and 623 K for 1 min under an N_2 atmosphere in a quartz tube.

2.2 Characterization

The structural properties of microwave heat treatment Sb_2Te_3 films, including the crystallinity, crystalline size, micro stain, and dislocation were investigated by X-ray

diffraction (PANalytical Empyrean) operating with copper radiation (Cu-Kλ ;α=0.154 nm). The data were recorded in the 2θ range of 10-60º. The surface morphology thickness and stoichiometry of the samples were obtained by Field emission scanning electron microscope and energy-dispersive X-ray spectroscopy (JEOL JSM-70 0 1F). The electrical properties including carrier concentration and mobility were investigated by Hall Effect measurement at room temperature (Ecopia, HMS3000) [10]. The Seebeck coefficient was simultaneously obtained by ZEM-3 (ULVAC-RIKO).

3. Results and discussion

The XRD patterns of Sb_2Te_3 films as a function of temperature using microwave-assisted DC magnetron sputtering technique are shown in Fig.1. As-deposited films can be indexed to a polycrystalline Sb_2Te_3 with a hexagonal structure (JCPDS # No. 15-0874) of (006), (009), (015), (1010), (110), (0015), (205) and (0018) orientations and no peak of elemental Sb and Te were observed. When the heating temperature increases, some minor diffraction peaks were expressed as a metallic Te (JCPDS # No. 36-1452). After increasing the heating temperature to 523K, the preferred orientation was intense and well-defined. It can be explained that microwave heating with a short duration of 1 min is more efficient to increase the ability of adatoms to move towards stable sites in lattice [11]. However, when the heat treatment raise to 573 and 623 K, the crystallinity of the samples is reduced. The crystalline size of Sb_2Te_3 films was calculated using Debye-Scherrer's equation.

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

Where D is crystallitesize, k is theconstant usually taken as 0.94, λ is thewavelength of X-ray radiation (0.154 nm), β is the full width at half maximum (FWHM) and θ is the diffraction angle.

The calculated results and XRD parameter are shown in Table.1. The crystalline size of the as-deposited film was 39.5 nm and was enlarged up to 42.2 nm with an increase in heating temperature to 523 K. The microstrain (ε) and dislocation density (ρ) of the films is considered by using Eq. (2) and (3).

$$\varepsilon = \frac{(\beta \cos\theta)}{4} \tag{2}$$

$$\rho = \frac{1}{D^2} \tag{3}$$

Table.1. Calculated the structural parameters of rapid microwave heat treatment Sb_2Te_3 films as a function of heating temperature.

Heating temperature (K)	FWHM (radian)	Crystalline size: D (nm)	Micro strain: $\boldsymbol{\varepsilon}$ ($\times 10^{-4}$ lines^{-2}/m^4)	Dislocation density: $\boldsymbol{\rho}$ ($\times 10^{14}$ lines/m^2)
As-dep	0.207	39.5	8.77	6.41
473	0.201	40.6	8.53	6.05
523	0.194	42.2	8.21	5.62
573	0.199	41.1	8.44	5.93
623	0.206	39.8	8.71	6.32

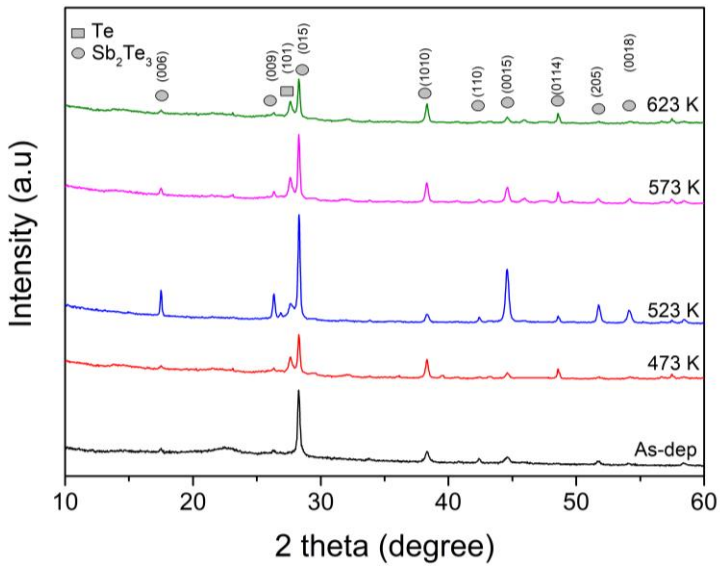

Fig. 1. XRD patterns of Sb_2Te_3 films as a function of microwave heating temperature for 1 min

Micro strain is used to define the disarrangement of lattice created during the deposition process which depends on sputtering parameters and the heat treatment process [16]. The decreasing of microstrain with increased heating temperature indicates better lattice arrangement in samples [16]. The dislocation has also described the imperfection inside the Sb_2Te_3 crystal structure [17], [18]. The reduction of the lattice imperfection was exhibited with an increase in heating temperature, which indicated that the high quality of the annealing films was obtained.

The surface morphologies of rapid microwave-assisted heat treatment Sb_2Te_3 film as a function of heating temperature were investigated by FE-SEM and displayed in Fig.2. Loose and vertical slices of as-deposited Sb_2Te_3 were obtained. The flakes are well crystallized with larger grains. During microwave heating temperature increases, and the heat is produced internally within the Sb_2Te_3 films, as an alternative to originating from an external heat source conventional [18]. Rapid heating in a short time leads to the energy of particles on the surface of Sb_2Te_3 films increasing. This process gives enough energy for the diffusion of the condensing particles, leading to lattice points forming an ordered crystalized structure agreeing with XRD results [10]. The grain of Sb_2Te_3 becomes a smaller flat flap and the porosity of the Sb_2Te_3 films is reduced as the heating temperature increases, which is expected to be beneficial for carrier transport.

The stoichiometric and thickness of rapid microwave annealing Sb_2Te_3 films were shown in Fig.3. It can be found that the Te concentration of as-deposited film was 58.7 at% and thickness was about 783 nm. This result indicates that Te concentration slightly decreased when the heating temperature increased. Typically, the vapor pressure of Te is higher than the vapor pressure of Sb [19]. It might be correlated with the change of non-stoichiometric Sb_2Te_3 films that occurred with increasing microwave thermal treatment. The short duration time of the microwave thermal treatment process was designed to prevent Te deficiency. The thickness of samples linearly decreased when the heating temperature increased. A dramatic decline in thickness with annealing temperature up to 623 K is associated with the reduction of porosity and smaller flat flaps of grain size of Sb_2Te_3 film.

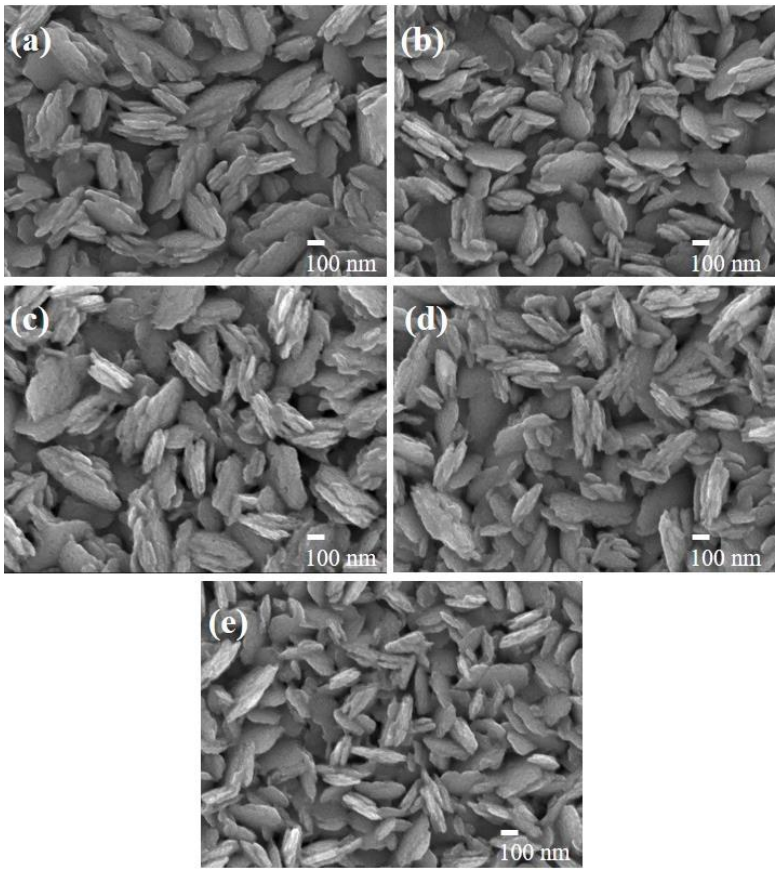

Fig. 2. Surface morphologies of microwave annealing (a) as-deposited, (b) 473 K, (c) 523 K, (d) 573 K, and (e) 623 K Sb_2Te_3 films for 1 min

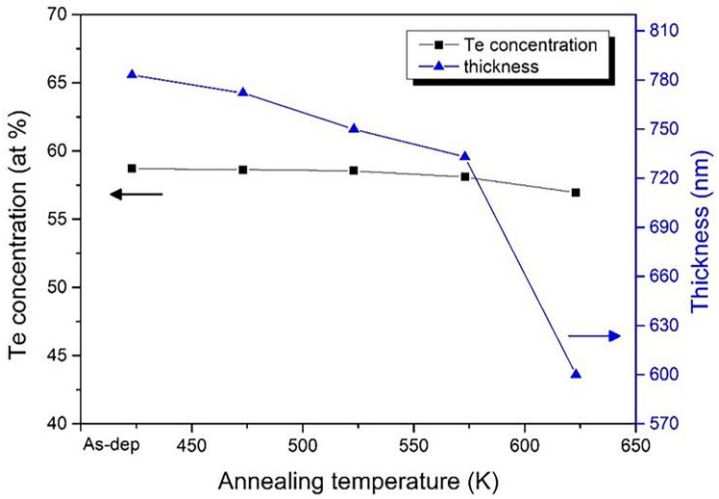

Fig. 3. Te concentration and thickness of Sb_2Te_3 film as a function of microwave heating temperature for 1 min

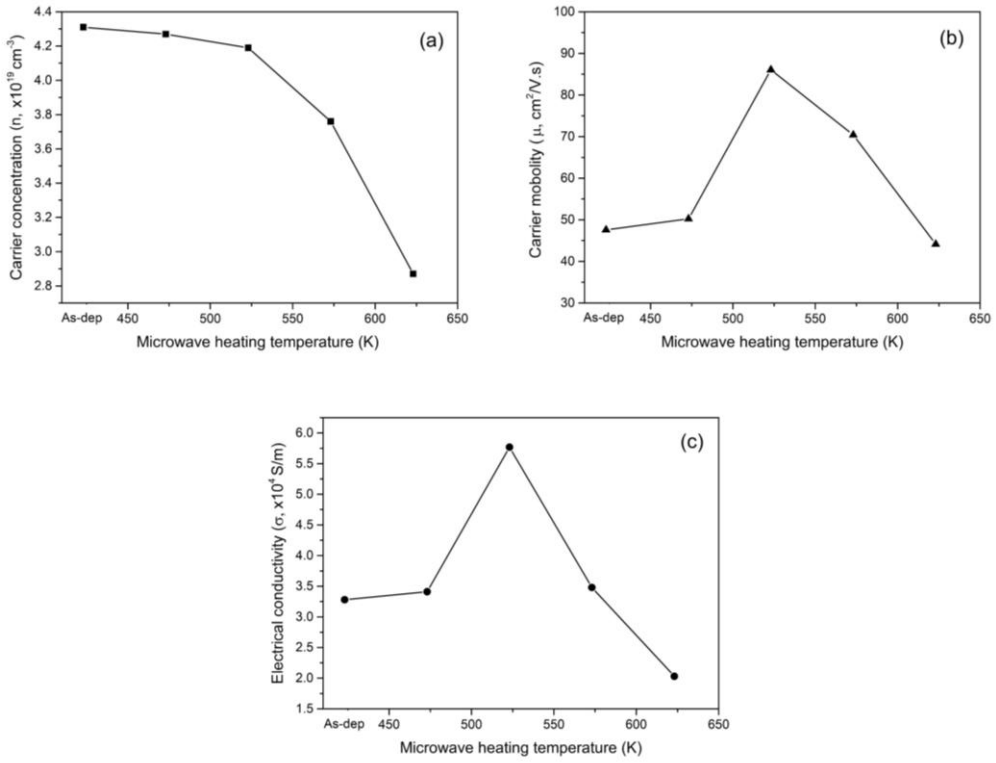

Fig. 4. (a) carrier concentration, (b) carrier mobility, and (c) electrical conductivity of Sb_2Te_3 films as a function of microwave heating temperature for 1 min

The electrical transport property of all samples was examined in Fig.4 as a function of heating temperature. All samples have a positive carrier concentration due to their p-type conductor, which is measured using Hall measurement. As shown in Fig. 4(a), the carrier concentration (η) of Sb_2Te_3 decreased from 4.31 to 2.87×10^{19} cm^{-3} with an increase in heating temperature. This result could be attributed to the reduction of point defects including the Sb'_{Te} antisite defect and Sb vacancies acting as acceptors in the Sb_2Te_3 lattice during the thermal treatment process [20]. The increase in carrier mobility (μ) of sample with a heating temperature rising to 523 K could be partly due to the reduction of point defect and partly due to crystallinity growth during the thermal treatment process as shown in Fig. 4(b). After the heating temperature rose over 523 K, the carrier mobility was dramatically dropped due to the flat flap of the small grain size of films (as shown with FE-SEM results in Fig.3), which contributed to the increased carrier scattering at the grain boundaries [21]. The electrical conductivity (σ) of the films increased from 3.28 to 5.77×10^4 S/m with a heating temperature rising to 523 K and then decreased by increasing the thermal treatment process temperature further by 623 K due to structural destruction. In general, the electrical conductivity depends on the crystallinity and the electrical transport property of the films given by Eq. (4).

$$\sigma = nq\mu \tag{4}$$

Where q is the electron charge. At a heating temperature of 523 K, the increased rate of carrier mobility was significantly higher than the decreased rate of carrier concentration. Therefore, the electrical conductivity of Sb_2Te_3 was enhanced [7].

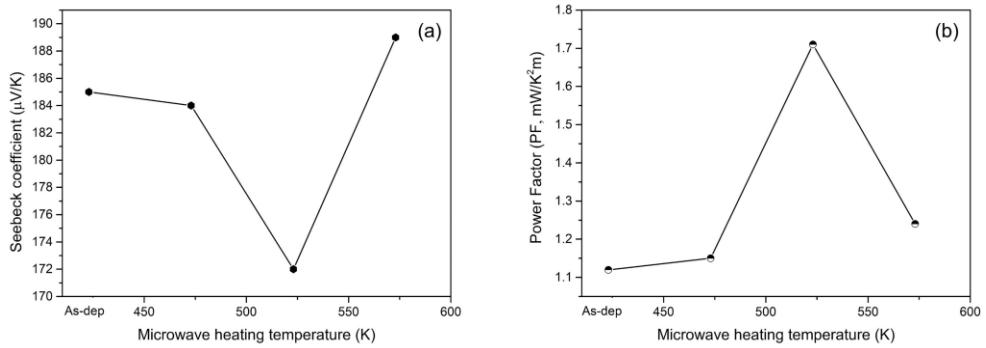

Fig. 5. (a) Seebeck coefficient and (b) power factor of Sb_2Te_3 films as a function of microwave heating temperature for 1 min

The thermoelectric properties of Sb_2Te_3 films were shown in Fig.5, which were improved by increasing the microwave heating temperature. The Seebeck coefficient values of all samples were positive indicating that all samples were p-type semiconductors. The Seebeck coefficient of the as-deposited films was improved by microwave thermal treatment as shown in Fig. 5(a). The power factor of Sb_2Te_3 films has been calculated by the Seebeck coefficient and the electrical conductivity. The as-deposited film has a value of 1.12 mW/K^{2}m. After microwave thermal treatment, the power factors increased dramatically. The highest value of the power factor of 1.71 mW/K^{2}m, which is annealed at 523 K for a short duration time of 1 min. Even though the higher annealing temperature above 523 K may lead to the deterioration of thermoelectric properties of the Sb_2Te_3 film [7].

4. Conclusion

The Sb_2Te_3 films were successfully deposited using rapid microwave-assisted DC magnetron sputtering on a polyimide flexible substrate. To enhance the structural, electrical, and thermoelectric properties and maintain the stoichiometry of the Sb_2Te_3 films, rapid microwave thermal treatment for 1 min in the temperature range from 473-623 K was carried out to produce the heat internally in the Sb_2Te_3 films. The crystallinity of Sb_2Te_3 films increases gradually with an increase in heating temperature. Meanwhile, the reduction of point defects including the antisite defect and Sb vacancies during the heating process. The thermal treatment process may effectively improve electrical transport properties. The power factor of the Sb_2Te_3 films reaches the highest value of 1.71 mW/K^{2}m, which is annealed at 523 K for a short duration of 1 min with a maximum electrical conductivity (5.77×10^4 S/m) and moderate Seebeck coefficient (172 μV/K). This is very promising for the realization of room-temperature thermoelectric applications with high performance.

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