Effect of Annealing Temperature on Properties of Co-Sputtered Bi$_2$Te$_3$

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Abstract. Bi$_2$Te$_3$ thin film samples are prepared by magnetron co sputtering. The samples are annealed in a nitrogen atmosphere and were treated at different temperature for 2 h. Effects of annealing temperature on the structure and thermoelectric properties of Bi$_2$Te$_3$ are studied in detail. As the annealing temperature increases, the Te element on the surface begins to volatilize, and some Te elements precipitate and crystallize on the surface, resulting in a decrease in the Te element in the Bi$_2$Te$_3$ thin film. When the annealing temperature is 350 °C, the power factor of Bi$_2$Te$_3$ film reaches a maximum of 0.21×10$^{-3}$ Wm$^{-1}$K$^{-2}$.

1. Introduction

Bi$_2$Te$_3$ based thermoelectric materials have been considered to be one of the best low-temperature thermoelectric materials and one of the most widely used thermoelectric materials in commercial products. Currently, Bi$_2$Te$_3$ nanoscale low-dimensional materials are processed by electrodeposition [1], magnetron sputtering [2], thermal evaporation [3], molecular beam epitaxy [4], pulsed laser deposition [5], etc. Compared with other methods, magnetron sputtering technology can be used for large-scale processing, with relatively simple equipment and processing processes, high film formation quality, relatively simple process conditions, and good compatibility with other MEMS processing processes. Therefore, magnetron sputtering technology has become the most attractive technology in the development of nano-material processing industry, and it is also the most likely to be applied to large-scale commercial sputtering processing systems.

Annealing can not only improve the crystalline state of the thermoelectric thin film and stabilize the structure of the thin film, but also adjust the thermoelectric properties of the thin film. S. Liu et al. prepared a Bi$_2$Te$_3$ film on a flexible substrate by magnetron sputtering and annealed it at different temperatures [6]. Bi$_2$Te$_3$ nanosheets appeared on the surface, which can be attributed to thermal stress. Compared with that before annealing, the ZT value of Bi$_2$Te$_3$ film was increased by more than 4 times. T. Talebi et al. prepared a p-type Bi$_2$Te$_3$ thin film by electrophoretic deposition [7], sintered at 693 K, and the in-plane Seebeck coefficient was 239 μVꞏK$^{-1}$ at 500 K. J. M. Lin et al. prepared a Bi$_2$Te$_3$ film on a silicon oxide substrate using a thermal evaporation method [8]. The maximum power factor obtained by annealing control was 6.05 μWꞏcm$^{-1}$ꞏK$^{-2}$. Z. Zeng et al. used co-sputtering to prepare Bi$_2$Te$_3$ films with different thicknesses on glass substrates[9], and studied the change in electrical conductivity of annealed films with different thicknesses (70~350 nm) with temperature.
This paper is based on the magnetron sputtering co-sputtering process to prepare Bi$_2$Te$_3$ thin film thermoelectric materials. The thermoelectric films are annealed at different temperatures, and the properties of the thin film are tested and analyzed.

2. Experiment

2.1. Substrate cleaning
The substrate used in this experiment is a Si substrate covered with a 1 μm thick SiO$_2$ oxide layer with a total thickness of 550 μm. The Si substrate was put into a mixed solution of concentrated sulfuric acid and hydrogen peroxide with a volume ratio of 3:1 and soak it for 10 min. Remove with tweezers, rinse with deionized water, and blow dry with dry compressed N$_2$. Then using an Ar ion source to perform back-sputter cleaning on the coated substrate, so that the surface of the substrate can be cleaned at the atomic level, thereby improving the bonding quality between the deposited film and the substrate.

2.2. Preparation and annealing of the film
The sputter deposition of Bi$_2$Te$_3$ thermoelectric thin film was co-sputtered. The Bi$_2$Te$_3$ thermoelectric thin film is deposited by means of Te (RF) + Bi (DC) co-sputtering, Te (RF) sputtering power was set to 10 W, Bi (DC) sputtering power was set to 13 W. The sputtering working pressure is set at 1.1 Pa by adjusting the high-purity argon flow rate. The deposited thin film samples were put into an annealing furnace for annealing treatment. First, the furnace cavity is evacuated. After the vacuum degree is lowered below 0.5 Pa, high-purity nitrogen is introduced to atmospheric pressure. Repeat three times to ensure nitrogen purity in the chamber. The samples were annealed with nitrogen at 200 °C, 250 °C, 300 °C, 350 °C, and 400 °C for 2 hours, and then allowed to cool to room temperature.

3. Result and Discussion

![XRD patterns of Bi$_2$Te$_3$ thin film at different annealing temperatures.](image)

Figure 1. XRD patterns of Bi$_2$Te$_3$ thin film at different annealing temperatures.

The XRD pattern of the Bi$_2$Te$_3$ thin film is shown in Figure 1, it is known that according to the data of Bi$_2$Te$_3$ (JCPDS 15-0863), Bi$_2$Te$_3$ has a layered rhombic structure with a space group of R-3m. The diffraction pattern of the Bi$_2$Te$_3$ film also has obvious diffraction peaks in the unannealed state, indicating that Bi$_2$Te$_3$ has good crystallinity. The main diffraction peaks of the diffraction pattern of Bi$_2$Te$_3$ thin film are (006), (015), (1, 0, and 10). The grains grow mainly in these three directions, and the diffraction peak intensity in the (015) direction is the strongest. When the annealing temperature is
400 °C, a (015) diffraction peak appears as the Te phase. With the increase of the annealing temperature, the intensity of the (006) and (1, 0, 10) diffraction peaks gradually increases, and their full width at half maximum gradually decreases, which can indicate that the grain size in these two directions is growing. For the (015) direction, when the annealing temperature is increased from 200 °C to 300 °C, the full width at half maximum of the diffraction peak gradually decreases. When the annealing temperature is 350 °C, the full width at half maximum of the diffraction peak increases. When the annealing temperature is 400 °C, the full width at half maximum of the diffraction peak decreases again. That is, when the annealing temperature is increased from 200 °C to 300 °C, the grain size in the (015) direction gradually increases. When the annealing temperature is 350 °C, the grain size decreases, and the annealing temperature is 400 °C. As the grain size increases again. When the annealing temperature is increased from 200 °C to 300 °C, the grain size increases, the grain boundaries decrease, the carrier scattering decreases, the carrier mobility increases, and the electrical conductivity increases. At 350 °C, due to the high temperature, Te volatiles and precipitates to form a nucleation centres, and Bi is in a molten state. When cooling, the precipitated Te is used as a nucleus to form a large number of new fine grains. When the annealing temperature is increased to 400 °C, the grain size formed by recrystallization increases. Due to the increase of phases in the (006) and (1, 0, 10) directions, the preferred orientation of the crystal grains in the film is destroyed due to the phase transition, and the disordered state of the crystal grains increases. As a result, carrier scattering is enhanced, and carrier mobility is reduced, thereby reducing the conductivity of the thin film.

The atomic ratio of Bi₂Te₃ film varying with different annealing temperature is shown in Figure 2. Before the annealing temperature was 200 °C, the ratio of the number of Te atoms and Bi atoms in the film remained basically stable. When the annealing temperature reached 250 °C, the proportion of Te atoms decreased. Continue to increase the temperature. When the temperature rises to 350 °C, the measured atomic ratio of Te atoms in the film increases. When the annealing temperature is increased to 400 °C, the number of Te atoms in the film decreases sharply. The main reason for the above changes may be that the element Te has a high vapor pressure. Due to the high vapor pressure of the Te element, it is easily volatile under vacuum conditions, especially at higher temperatures. However, in this experiment, under the normal pressure of nitrogen, the Te element remained relatively stable at a lower annealing temperature (200 °C), and the proportion of Te atoms in the film was basically stable. However, with the increase of the annealing temperature, the Te element on the surface of the film began to volatilize, and some Te elements precipitated and crystallized on the surface of the film, resulting in a decrease in the Te element in the film. As the annealing temperature continues to increase, the deeper Te element precipitates on the surface and forms holes in the film. At the same time, Te rapidly grows and deposits on the film surface, and the Te precipitates grow up. Te particles grow on the surface of the film, and the particle size is equivalent to the thickness of the film. The distribution of particles of this size on the surface of the film causes the Te element to be concentrated.

**Figure 2.** The atomic ratio of Bi₂Te₃ film varying with different annealing temperature.
near the surface of the film. As a result, the Te atomic ratio obtained by surface scanning showed an increase. When the annealing temperature is increased to 400 °C, a large amount of Te element in the film is volatilized. As the temperature is too high, the Te element is volatilized seriously, and large holes are formed in the film. A large part of the volatile Te element is deposited on the inner wall of the annealing furnace cavity, and a part of the Te element precipitates and grows on the film surface. Due to the large film loss, the Te atomic ratio of the film is greatly reduced.

![Figure 3](image-url)

**Figure 3.** Relationship of properties of Bi$_2$Te$_3$ film and annealing temperature: (a) carrier concentration and carrier mobility, (b) conductivity and Seebeck coefficient.

Annealing not only affects the composition of the film, but also affects the properties of the film. The thermoelectric properties of the film vary with the annealing temperature as showed in Figure 3. The electrical conductivity of Bi$_2$Te$_3$ film increased with the increase of annealing time and reached the maximum value at an annealing temperature of 350 °C. The conductivity of Bi$_2$Te$_3$ film increased from $0.73 \times 10^4$ Sm$^{-1}$ at 200 °C to $1.16 \times 10^4$ Sm$^{-1}$. However, when the annealing temperature is increased to 400 °C, there is a significant decrease. The conductivity of the Bi$_2$Te$_3$ film is reduced to $0.98 \times 10^4$ Sm$^{-1}$. If $\mu$ is conductivity, $n$ is carrier concentration and $e$ is carrier charge. Then the carrier mobility can be expressed as:

$$\mu = \frac{\sigma}{ne} \quad (1)$$

It can be known from (1) that the increase in electrical conductivity may be due to the increase in annealing temperature, the crystal growth has a preferred orientation, and the growth of grains results in the reduction of grain boundaries. Reduced mobility. When the annealing temperature is too high, more crystal defects may be caused by the loss of Te atoms, which results in enhanced carrier scattering and reduced carrier mobility, resulting in a decrease in conductivity. It can be seen from Figure. 3 (b) that the absolute value of Seebeck coefficient increases with the increase of annealing temperature and reaches a maximum value at 350 °C. The absolute value of Seebeck coefficient of Bi$_2$Te$_3$ film material increased from 108.8 $\mu$V/K to 134.4 $\mu$V/K. When the annealing temperature is increased to 400 °C, the absolute value of Seebeck coefficient of Bi$_2$Te$_3$ thin film material decreases to 127.9 $\mu$V/K.

The electrical properties of thermoelectric materials can be expressed by power factor ($PF$):

$$PF = S^2 \sigma \quad (2)$$

Where, $S$ is the Seebeck coefficient of thermoelectric material, and $\sigma$ is the conductivity of thermoelectric material. The power factor of Bi$_2$Te$_3$ thin film varies with the annealing temperature of
the material as showed in Figure 4. The power factor of Bi$_2$Te$_3$ film increased with the increase of annealing temperature, and reached the maximum value of $0.21 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$ at 350 °C.

Figure 4. The relationship between the power factor and annealing temperature of Bi$_2$Te$_3$ films

4. Conclusion
In this paper, the preparation of Bi$_2$Te$_3$ thin films by magnetron co-sputtering is studied. The effects of annealing temperature on the chemical composition and electrical properties of materials were studied. Under conditions of 13 W DC Bi target and 10 W RF Te target, the ratio of the number of Bi atoms to Te atoms is close to 2:3 when the working pressure is 1.1 Pa. The annealing temperature can cause the change of the atomic metrology ratio and the electrical properties of the thermoelectric films. When the annealing temperature is 350 °C, the power factor of Bi$_2$Te$_3$ film reaches the maximum value, which is $0.21 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$.

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