Ion Beam Irradiation Effect on Thermoelectric Properties of Bi_2Te_3 and Sb_2Te_3 Thin Films

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Abstract

Thermoelectric energy harvesting is a very promising application in nuclear power plants for self-maintained wireless sensors. However, the effects of intensive radiation on the performance of thermoelectric materials under relevant reactor environments such as energetic neutrons are not fully understood. In this work, radiation effects of bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) thermoelectric thin film samples prepared by E-beam evaporation are investigated using Ne^{2+} ion irradiations at different fluences of 5×10^{14} , 10^{15} , 5×10^{15} and 10^{16} ions/cm² with the focus on the transport and structural properties. Electrical conductivities, Seebeck coefficients and power factors are characterized as ion fluence changes. X-ray diffraction (XRD) and transmission electron microscopy (TEM) of the samples are obtained to assess how phase and microstructure influence the transport properties. Carrier concentration and Hall mobility are obtained from Hall effect measurements,

which provide further insight into the electrical conductivity and Seebeck coefficient mechanisms. Positive effects of ion irradiations from Ne^{2+} on thermoelectric material property are observed to increase the power factor to 208% for Bi_2Te_3 and 337% for Sb_2Te_3 materials between fluence of 1 and $5 \times 10^{15}/\text{cm}^2$, due to the increasing of the electrical conductivity as a result of ionization radiation-enhanced crystallinity. However, under a higher fluence, $5 \times 10^{15}/\text{cm}^2$ in this case, the power factor starts to decrease accordingly, limiting the enhancements of thermoelectric materials properties under intensive radiation environment.

Keywords: thermoelectric, ion beam radiation, bismuth telluride, antimony telluride, thin film, carrier mobility

1 Introduction

Thermoelectric generator allows the direct solid-state conversion between thermal and electrical energy^[1], which are of particular interest for waste heat recovery^[2], improved energy efficiency^[3], and powering of remote sensors and electronics^[4]. Among the many potential applications, thermoelectrics for power harvesting in nuclear power plants for sensors and sensing networks are especially attractive since heat is available at a variety of locations.

Nuclear plants accidents (Chernobyl, Three Mile Island, and Fukushima Daiichi) have casted a shadow on the history and future of nuclear power. Safety thus rightfully remains an enormous concern in the development and operations of nuclear power plants and fuel cycles. In the Fukushima event, one major concern was a total loss of power at the plant, leading to catastrophic failure of reactor systems and loss of coolants. As a result, sensing and actuation systems stopped working. Increasingly research is going on recently to develop thermoelectric-driven sensing technologies to power sensor and communication packages in the event of

1 massive power loss. Lin *et al* ^[5] discussed the development of an independently powered sen-
2 sor network that uses thermoelectric generators (TEGs) to provide power for monitoring and
3 actuation in blackout situations for small modular reactors. Carstens *et al* ^[6] proposed using
4 TEGs to power wireless sensors to monitor spent nuclear fuel during dry-cask storage. Clay-
5 ton *et al* ^[7] developed and demonstrated an advanced, multifunctional, power-scavenging
6 sensor network system for nuclear power plants.

7 Several recent studies have reported on the radiation effect on thermoelectric material,
8 thermoelectric module and related power electronics. Back to 1960s, Corelli *et al* ^[8] reported
9 the radiation from the spent fuel can affect the physical properties of the thermoelectric mate-
10 rials, which then influence the power production from the TEG. At 1961, Kilp *et al* ^[9] re-
11 ported, when the thermoelectric material was irradiated at reactor ambient temperatures, in-
12 crease of electrical resistivity and Seebeck coefficient but overall reduction of the power fac-
13 tor. Carstens *et al* ^[6] reported gamma radiation effect on the commercial Hi-Z modules in
14 which they used bismuth telluride based alloy and DC-DC converters. The results showed
15 that TEG was not affected by gamma radiation at a dose rate of 170 Rad/min; while DC-DC
16 converter could not operate normally at the presence of gamma radiation. Up to now, few re-
17 searchers studied neutron radiation effects on thermoelectric materials.

18 However, high neutron dose radiation test is not practical due to limited neutron irradi-
19 ation access as well as the complexity of post irradiation testing. As an alternative investiga-
20 tion method, ion beam irradiation has been used to simulate the radiation damage caused by
21 primary knocked atoms (PKA) upon the interaction of energetic neutrons with materials. Due
22 to the higher and more controllable ion dose rate, the radiation experiment can be completed
23 in a much shorter period due to much higher damage efficiency of energetic ion beams as
24 compared with neutrons. The radiation damage level in terms of displacements per atoms can

1 be simulated using SRIM codes, allowing simulation of radiation damages of the primary
2 knocked atoms (PKAs) upon energetic neutron-atoms interaction. The properties changes of
3 materials can be correlated with the displacement damage levels.

4 Among the few research work of ion radiation on thermoelectric, Kubiak *et al*^[18] re-
5 ported effect of 350 eV He+, Ar+ and Xe+ bombardment of PbTe. They concluded in the case
6 of Ar+ and Xe+ bombardment the altered layer appears to extend over a depth commensurate
7 with the ion range, the results for He+ bombardment suggest that only the very surface is
8 depleted of Te. Budak *et al*^{[20], [21]} reported MeV Si ion beam modification effects on the
9 thermoelectric generator from Er_{0.1}Fe_{1.9}SbGe_{0.4} and SiO₂/SiO₂ + Ge nanolayers thin film.
10 Guner *et al*^[22] studied effects of MeV Si ions bombardment on the thermoelectric properties
11 of Zn₄Sb₃ and CeFe₂Co₂Sb₁₂ thin films. Zheng *et al*^{[23], [24]} reported improvement on ther-
12 moelectric properties of multilayered multilayer super-lattice by MeV Si ion beam bombard-
13 ment.

14 In this work, the properties of thin films Bi₂Te₃/Sb₂Te₃ grown using e-beam evapora-
15 tion and irradiated using Ne²⁺ ion are reported. Structural properties for ion beam irradiated
16 Bi₂Te₃/Sb₂Te₃ thin films are presented. Also, the influence of Ne²⁺ ion fluence level on crys-
17 tallinity and defect accumulation for both samples are discussed. Measurements of electrical
18 conductivity, Seebeck coefficient, carrier concentration and mobility are performed on ion
19 bombarded samples with different fluences. For reference as-grown thin films are also cha-
20 racterized and compared to the ion-bombarded samples. An ionization radiation-induced de-
21 fect recovery and reorientation were observed for both films as evidenced by XRD and TEM.
22 A competition of the ionization radiation and displacement damage dominates the variations
23 of the electrical and thermoelectrical properties of materials. Positive effects of ion irradi-
24 tions from Ne²⁺ on thermoelectric materials are observed, which increases the power factors

of Bi₂Te₃ and Sb₂Te₃ materials, respectively, consistent with the increase of the electrical conductivity as a result of ionization radiation-enhanced crystallinity.

2 Experiment and Methods

Thermoelectric performance is characterized by the dimensionless figure of merit $ZT = \sigma S^2 T / \kappa$ and power factor $PF = \sigma S^2$ where S is the Seebeck coefficient (V/K), σ is the electrical conductivity (S/m), κ is the thermal conductivity (W/m·K), and T is the absolute temperature in Kelvin (K). The electrical conductivity $\sigma = ne\mu$ is given by carrier concentration n , carrier mobility μ and electron charge e . Carrier concentration and mobility can be determined by measuring the Hall coefficient R_H . For materials in which electrons are the primary carriers, $R_H = -1/ne$. Combining the Hall effect coefficient and electrical conductivity, the mobility of such materials can be expressed as $\mu = -\sigma R_H$. An expression for the Seebeck coefficient for n -type thermoelectric material is obtained by Busch and Winkler^[25] as

$$S = -\frac{k}{e} \left(\frac{5}{2} + r - \ln \frac{n}{N_c} \right). \quad (1)$$

Here k is Boltzmann's constant, r is the exponent of the power function in the energy-dependent relaxation time expression^[26], and N_c is the effective density of states in the valence band. As can be seen, the Seebeck coefficient is affected by carrier concentration, n .

Three-inch-diameter boron-doped p-type <100> silicon wafers (Montoco Silicon Technologies, Inc.) are used as the substrates in this research. The silicon wafers are 350- to 400-μm-thick and the resistivity is in 1 to 5 Ω·cm range. The wafers are initially oxidized at 1100 °C for 60 mins to get a 0.5-μm-thick silicon dioxide layer using wet thermal oxidation.

1 The Bi_2Te_3 and Sb_2Te_3 thin films are grown by e-beam evaporation deposition, using a Kurt
2 J. Lesker PVD 75 E-beam/thermal evaporation system. Solid antimony (III) telluride and
3 bismuth (III) telluride (99.999 % purity; Alfa Aesar Company) are evaporated for growth of
4 the Bi_2Te_3 and Sb_2Te_3 thin films, respectively. The films are deposited at room temperature
5 without substrate heating. The process chamber has a background pressure of 2×10^{-7} Torr.
6 The thickness of Bi_2Te_3 and Sb_2Te_3 thin films is controlled by an INFICON deposition moni-
7 tor during the deposition, and measured by Stylus Profilometry (Bruker, IL, USA). Table 1
8 summarizes all of the samples grown by e-beam evaporation and ion beam irradiation condi-
9 tions.

10 The ion beam irradiations on thin film samples are performed at Ion Beam Lab of Los
11 Alamos National Laboratory with 0.4 MeV Ne^{2+} ions using a 200 kV ion implanter. The ion
12 irradiation is performed at room temperature without sample titling, and the samples are irra-
13 diated at different fluences from 0.5×10^{15} , 1×10^{15} , 5×10^{15} and 10×10^{15} ions/ cm^2 . The ion
14 fluences are also converted to the unit of displacements per atom (dpa) using the Stopping
15 and Range of Ions in Matter (SRIM)-2008 program based on the Kinchin-Pease model and
16 full cascade calculations (Table 1) using a displacement energy of 25 eV for every atom.

1

2 The phase composition of the samples before and after irradiations was analyzed with X-ray
 3 diffraction (XRD) (Ultimate III, Rigaku, TX, USA) utilizing Cu K α radiation and energy-
 4 dispersive X-ray spectroscopy (EDS) (JEOL 7600F, Tokyo, JP). The cross-section morphol-
 5 ogies of the sample were observed using a transmission electric microscope (TEM) (JEOL
 6 1400, Tokyo, JP). The electrical conductivity was measured using a Keithley digital multime-
 7 ter (Model 2700, Keithley Instruments, Inc., OH, USA) and heated from 300 to 400 K using a
 8 High Temperature Probe Station (MBE-Komponenten AO500,, Germany). Seebeck coeffi-
 9 cients were measured using a differential method under vacuum. To investigate its contribu-
 10 tion to electrical conductivity, the carrier concentration and Hall mobility were measured
 11 with a Hall Measurement System (8404, Lake Shore Cryotronics, Inc., OH, USA) using the
 12 Van der Pauw method.

13 3 RESULTS AND DISCUSSIONS

14 3.1. Phase composition of Bi₂Te₃ and Sb₂Te₃ before and after ion beam irradiation

15

16 **FIG. 1. XRD of Bi₂Te₃ (a) and Sb₂Te₃ (b) thin film before and after ion beam irradiation shows an irradiation-**
 17 **induced reorientation and enhancement of crystallinity as the ion fluence increases**

1 Figure 1 shows the XRD patterns of Bi_2Te_3 and Sb_2Te_3 thin films before and after ion bom-
2 bardment. Sample N0 and P0 were as-grown *n*-type Bi_2Te_3 and *p*-type Sb_2Te_3 samples using
3 e-beam evaporation; while the rest samples were bombarded with Ne^{2+} ion at different total
4 fluences. For Bi_2Te_3 , the as-grown thin film showed main phase orientation at direction
5 (015). Upon 400 keV Ne ion irradiation, no irradiation-induced amorphization was observed,
6 and both Bi_2Te_3 and Sb_2Te_3 samples remain highly crystalline as revealed by the XRD pat-
7 terns. The increase in the ion fluence will further increase the crystallinity as evidenced by
8 the peak narrowing of the XRD patterns. Additionally, an irradiation-induced reorientation
9 occurred for both thin films, as evidenced by the increased intensity of the XRD diffraction
10 peaks of (006) and (0015) for Bi_2Te_3 (Fig. 1a). A similar behavior was observed for Sb_2Te_3
11 film (see Fig. 1b). Before ion beam irradiation, the as-grown sample is located at mainly
12 (015) direction and after the irradiation secondary preferred orientation in the direction of
13 (009) is clearly visible as ion fluence increases.

14 The energy loss mechanism of the energetic ions is crucial in determining the irradi-
15 ation damage process. The ballistic effect of nuclear energy loss (or nuclear stopping power:
16 S_n) causes atomic displacements that can lead to amorphization of the irradiated materials. On
17 the other hand, ionization radiation can promote defect recombination or recovery, even re-
18 crystallization of materials. A higher ENSP (electron to nuclear stopping power ratio) value
19 may result in higher radiation defect recovery rate as compared with radiation damage accu-
20 mulation, and hence enhanced radiation resistance. The radiation-enhanced crystallinity and
21 reorientation of the thermoelectric thin films upon 400 keV Ne^{2+} suggests that the ionization
22 radiation dominated radiation damage process. This is consistent with the relatively small
23 displacement damage created by the Ne^{2+} ions even at the highest ion fluences (1.87 and 1.49
24 dpa for Bi_2Te_3 and Sb_2Te_3 , respectively), and significantly higher electronic energy loss S_e

and greater ENSP ratios for both Bi_2Te_3 and Sb_2Te_3 . The ionization-radiation enhanced crystallinity and reorientation may also lead to the reduction of the defects upon irradiation and thus increases in the electrical conductivity upon initial ion irradiation as elaborated later.

3.2. TEM of Bi_2Te_3 and Sb_2Te_3 before and after ion beam irradiation

FIG. 2. TEM of Bi_2Te_3 a) before radiation N0, b) after radiation N3 and Sb_2Te_3 c) before radiation P0, d) after radiation P3

Figure 2 shows the TEM images and diffraction patterns of two type samples before and after ion irradiation. The FIG. 2(a) shows a high magnificant TEM of as grown Bi_2Te_3 and FIG. 2 (b) shows the TEM of Bi_2Te_3 after 5×10^{15} ions/cm² ion radiation N3 sample. As shown, the grain size increases in N3 suggesting the ionization radiation-induced defect recovery and grain growth, consistent with the XRD patterns. The selected electron diffraction

1 pattern (SAED) of the as-grown Bi_2Te_3 film (inset in Fig. 2a) shows a ring pattern, a charac-
2 teristic feature of the nanocrystalline materials. A preferred orientation was observed as
3 shown by the arc in the SAED which can be indexed as the (015) spacing based on structural
4 data of Bi_2Te_3 (PDF#15-0874). Upon ion irradiation, the SAED pattern consists of discrete
5 diffraction spots, inferring increased grain size upon ion irradiation. The originally preferred
6 orientation of the (015) disappeared despite radiation-induced reorientation was observed,
7 probably due to the different zone axis of the SAED pattern. Similar behavior occurred for
8 Sb_2Te_3 film upon irradiation. Before irradiation, the Sb_2Te_3 thin film has a low degree of
9 crystallinity, and nano-sized particles were embedded into an amorphous-dominated matrix
10 (Fig. 2c). The selected electron diffraction pattern (SAED) of the as-grown Sb_2Te_3 film (inset
11 in Fig. 2c,d) also shows a low degree of crystallinity. Ion irradiation significantly improves
12 the crystallinity of the material as a result of the ionization radiation-induced defect recovery
13 process. Overall, N type Bi_2Te_3 sample has better crystallinity than P type Sb_2Te_3 and TEM
14 results are well correlated with XRD results showed before. The orientation changes after ion
15 radiation implies the randomization happens during the process.

16 **3.3. Transport properties of Bi_2Te_3 and Sb_2Te_3**

17 **1) Electrical conductivity variation upon ion irradiation**

18 Electrical resistivity measurements were made from 300 to 400 K under vacuum. The meas-
19 ured electrical conductivities for both samples are shown in Figure 3, which indicates that the
20 variation in electrical conductivity is significant upon ion radiation. In Figure 3(a), N0 which
21 was as-grown sample, has a slightly higher resistivity than the rest Bi_2Te_3 samples with ion
22 beam irradiations. For the Sb_2Te_3 thin film sample, the trend is similar as Bi_2Te_3 sample: P0
23 has higher electrical resistivity than P1~P4 upon ion beam irradiation, which is again likely
24 due to the radiation induced ionization during ion radiation process. The decrease of electrical

1 resistivity of both samples with increase of temperature is of the intrinsic semiconductor cha-
 2 racter.

3
 4 **FIG. 3. Electrical resistivity of Bi_2Te_3 (a) and Sb_2Te_3 (b) thin film after bombardment decrease to some extent and**
 5 **then increase after the ion fluence of $5 \times 10^{15} \text{ ions/cm}^2$**

6 Figure 4 shows the variation of the electrical conductivity as a function of ion fluence.
 7 For both films, the as-grown samples have higher resistivities than the materials after ion
 8 beam irradiation, consistent with lower carrier concentration as referred from Hall Effect
 9 measurements (Table 3). The improved electrical conductivity of both films with increased
 10 fluences may be attributed to the ionization-induced recovery of the intrinsic defects during
 11 film deposition process, and thus enhancement of the carrier concentration. With further in-
 12 crease of ion fluence above $5 \times 10^5 \text{ ions/cm}^2$, the electrical conductivity decreases for both N4
 13 and P4 samples as a result of the accumulation of displacement-induced defects in the thin
 14 film in which the displacement damage dominates over the ionization radiation.

FIG. 4. Room temperature electrical conductivity for Bi₂Te₃ and Sb₂Te₃ samples at various ion fluences

In order to understand the mechanisms and key parameters that affect electrical conductivity, Hall effect measurements at room temperature were made with van der Pauw method and the results are shown in Table 3. The as-grown Bi₂Te₃ and Sb₂Te₃ thin film (N0 & P0) have lower carrier mobility than those of ion beam irradiated samples. As ion fluence increases before 5×10^{15} ions/cm², the carrier mobility in both Bi₂Te₃ and Sb₂Te₃ sample increases due to radiation induced defect recovery process showed in XRD result (see FIG. 1). After the ion fluence reaches 5×10^{15} ions/cm², higher fluence starts to decrease the mobility which may come from the accumulated defects generated by ion radiation. In Table 3, the carrier concentration of the Bi₂Te₃ and Sb₂Te₃ samples starts to decrease at the beginning of ion radiation and it turns reversely at higher fluence. The carrier concentration by Hall effect measurements matches well with the electrical resistivity using four-probe machine at room temperature. The change of the carrier concentration may also be associated with the mini-bands formation during ion radiation process.

1

Table 3. Room temperature Hall Effect for two type thin film at different fluence

Sample	Carrier concentration n ($10^{20}/\text{cm}^3$)	Hall mobility μ ($\text{cm}^2/\text{V}\cdot\text{s}$)	Conductivity $\bullet = ne\mu$ ($\text{S/m} \times 10^5$)
N0	5.78	1.50	1.4
N1	5.45	2.20	1.9
N2	5.11	2.74	2.3
N3	5.46	3.29	2.9
N4	5.04	2.66	2.2
P0	3.31	2.80	1.5
P1	3.23	3.50	1.8
P2	3.03	5.46	2.7
P3	3.18	5.50	2.8
P4	3.25	3.21	1.7

2

3 The samples in this study are non-stoichiometric and polycrystalline. The mobility is
4 far less than that of stoichiometric $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ single crystal, e.g., mobility of 313
5 $\text{cm}^2/\text{V}\cdot\text{sec}$ for thin films Bi_2Te_3 using metalorganic chemical vapor deposition^[27] and 400
6 $\text{cm}^2/\text{V}\cdot\text{sec}$ for single crystal bulk Sb_2Te_3 ^[28]. Generally, mobility is determined by phonon
7 scattering at high temperatures and ionized impurity scattering at low temperatures for semi-
8 conductor materials.^[29] For our samples, the increase of crystallization shown in XRD ac-
9 count for the increase of mobility and at higher fluence the accumulated defects decreased the
10 mobility.

11

2) Seebeck coefficient

FIG. 5. Seebeck of Bi_2Te_3 (a) and Sb_2Te_3 (b) thin film before and after ion bombardment

Figure 5 shows the measured Seebeck coefficients of Bi_2Te_3 and Sb_2Te_3 thin films before and after bombardment. Seebeck coefficient is very sensitive to carrier concentration and inversely proportional to electrical conductivity due to the opposite dependence of carrier concentration, i.e., $S \sim \ln(n)$ in Eq. (1).^[25] Figure 5(a) shows that the un-irradiated sample N0 has a lower Seebeck coefficient because of its higher carrier concentration. As ion fluence increases from N0 to N2, the Seebeck coefficient increases since the carrier concentration continues to decrease. Figure 5(b) shows the similar trends for Sb_2Te_3 samples as P0 has a much higher carrier concentration than P1-P4. Generally as temperature increases, the Seebeck coefficient will increase in magnitude because the ratio N_c/n in Eq. (1) is proportional to $\exp(kT)$. The fact that the Seebeck coefficient is negative in Figure 5(a) indicates that Bi_2Te_3 is an n -type semiconductor, and the positive Seebeck value in Figure 5(b) shows Sb_2Te_3 is a p -type semiconductor. This observation is consistent with the Hall effect measurement.

3) Power factor (PF)

FIG. 6. Room temperature PF of Bi₂Te₃ and Sb₂Te₃ thin film increases when ion fluence increases and the peak achieves between 1 x10¹⁵ ions/cm² and 5x10¹⁵ ions/cm²

The power factor value $PF=S^2\sigma$ of the sample can be estimated by combining the in-plane electrical properties σ and the in-plane Seebeck coefficient S . Figure 6 shows the in-plane power factors for Bi₂Te₃ and Sb₂Te₃ thin films before and after ion irradiation. Positive effects of ion irradiations from Ne²⁺ on thermoelectric material property are observed because of large improvements in electrical conductivity and Seebeck coefficient caused by carrier concentration and mobility change. Figure 6 shows the maximum PF for Bi₂Te₃ appeared at 5x10¹⁵ ions/cm² Ne ion fluence, which increased to 208% compared with sample before ion radiation. For Sb₂Te₃ the maximum PF occurred at 1x10¹⁵ ions/cm² Ne²⁺, which increased to 337% compared with sample before radiation. However, under a higher fluence, 5x10¹⁵ ions/cm² for Bi₂Te₃ and 1x10¹⁵ ions/cm² for Sb₂Te₃, the power factor start to decrease accordingly, limiting the enhancements of thermoelectrical materials properties under intensive

1 radiation environment. This is because at higher fluence, the mobility becomes smaller as the
2 accumulation of defects generated by displacement damages to the materials and eventually
3 the electrical conductivity starts to decrease.

5 **4 CONCLUSIONS**

6 In conclusion, thermoelectric Bi₂Te₃ and Sb₂Te₃ thin films prepared by E-beam eva-
7 poration were irradiated by 400 keV Ne²⁺ in order to investigate the radiation effects of the
8 thermoelectrical materials as energy harvester in nuclear environment. The microstructure
9 evolution, phase/crystallinity and the thermoelectrical properties were systematically investi-
10 gated. An ionization radiation-induced defect recovery and reorientation were observed for
11 both films as evidenced by XRD and TEM. A competition of the ionization radiation and dis-
12 placement damage dominates the variations of the electrical and thermoelectrical properties
13 of materials. The electrical resistivity decreases in both materials upon ion irradiation due to
14 the increase in carrier mobility and better crystallinity. The accumulated defects induced by
15 displacement damage at higher ion fluence eventually result in the reduction of the mobility
16 and electrical conductivity. Seebeck coefficient increases accordingly with ion radiation due
17 to the reduction of carrier concentration and the charge mobility. Positive effects of ion irradi-
18 ations from Ne²⁺ on thermoelectric materials are observed, which increases the power factors
19 to 208% for Bi₂Te₃ and 337% for Sb₂Te₃ materials, respectively, consistent with the increase
20 of the electrical conductivity as a result of ionization radiation-enhanced crystallinity. How-
21 ever, under a higher fluence, the power factor starts to decrease, limiting the enhancements of
22 thermoelectrical material properties under intensive radiation environment.

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