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Ion beam irradiation effect on thermoelectric properties of Bi_2Te_3 and Sb_2Te_3 thin films

Gaosheng Fu [a], Lei Zuo [a,b,*], Jie Lian [c], Yongqiang Wang [d], Jie Chen [b], Jon Longtin [a], Zhigang Xiao [e]

[a] Department of Mechanical Engineering, Stony Brook University, Stony Brook, NY 11794, United States
[b] Department of Mechanical Engineering, Virginia Tech, Blacksburg, VA 24061, United States
[c] Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States
[d] Materials Science & Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87544, United States
[e] Department of Electrical Engineering, Alabama A&M University, Normal, AL 35762, United States

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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/cm^2 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 5×10^{15} cm^2, due to the increasing of the electrical conductivity as a result of ionization radiation-enhanced crystallinity. However, under a higher fluence, 5×10^{15} cm^2 in this case, the power factor starts to decrease accordingly, limiting the enhancements of thermoelectric materials properties under intensive radiation environment.

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

Several recent studies have reported on the radiation effect on thermoelectric material, thermoelectric module and related power electronics. Back to 1960s, Corelli et al. [8] reported the radiation from the spent fuel can affect the physical properties of the

* Corresponding author.
E-mail address: leizuo@vt.edu (L. Zuo).

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thermoelectric materials, which then influence the power production from the TEG. At 1961, Kilp et al. [9] reported, when the thermoelectric material was irradiated at reactor ambient temperatures, increase of electrical resistivity and Seebeck coefficient but overall reduction of the power factor. Carstens et al. [6] reported gamma radiation effect on the commercial Hi-Z modules in which they used bismuth telluride based alloy and DC–DC converters. The results showed that TEG was not affected by gamma radiation at a dose rate of 170 Rad/min; while DC–DC converter could not operate normally at the presence of gamma radiation. Up to now, few researchers studied neutron radiation effects on thermoelectric materials.

However, high neutron dose radiation test is not practical due to limited neutron irradiation access as well as the complexity of post irradiation testing. As an alternative investigation method, ion beam irradiation has been used to simulate the radiation damage caused by primary knocked atoms (PKA) upon the interaction of energetic neutrons with materials. Due to the higher and more controllable ion dose rate, the radiation experiment can be completed in a much shorter period due to much higher damage efficiency of energetic ion beams as compared with neutrons. The radiation damage level in terms of displacements per atoms can be simulated using SRIM codes, allowing simulation of radiation damages of the primary knocked atoms (PKAs) upon energetic neutron-atoms interaction. The properties changes of materials can be correlated with the displacement damage levels.

Among the few research work of ion radiation on thermoelectric, Kubiak et al. [10] reported effect of 350 eV He^+, Ar^+ and Xe^+ bombardment of PbTe. They concluded in the case of Ar^+ and Xe^+ bombardment the altered layer appears to extend over a depth commensurate with the ion range, the results for He^+ bombardment suggest that only the very surface is depleted of Te. Budak et al. [11,12] reported MeV Si ion beam modification effects on the thermoelectric generator from $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ and SiO_2/SiO_2 + Ge nanolayers thin film. Guner et al. [13] studied effects of MeV Si ions bombardment on the thermoelectric properties of Zn_4Sb_3 and $CeFe_2Co_2Sb_{12}$ thin films. Zheng et al. [14,15] reported improvement on thermoelectric properties of multilayered multilayer super-lattice by MeV Si ion beam bombardment.

In this work, the properties of thin films Bi_2Te_3/Sb_2Te_3 grown using e-beam evaporation and irradiated using Ne^{2+} ion are reported. Structural properties for ion beam irradiated Bi_2Te_3/Sb_2Te_3 thin films are presented. Also, the influence of Ne^{2+} ion fluence level on crystallinity and defect accumulation for both samples are discussed. Measurements of electrical conductivity, Seebeck coefficient, carrier concentration and mobility are performed on ion bombarded samples with different fluences. For reference as-grown thin films are also characterized and compared to the ion-bombarded samples. An ionization radiation-induced defect recovery and reorientation were observed for both films as evidenced by XRD and TEM. A competition of the ionization radiation and displacement damage dominates the variations of the electrical and thermoelectrical properties of materials. Positive effects of ion irradiations from Ne^{2+} on thermoelectric materials are observed, which increases the power factors of Bi_2Te_3 and Sb_2Te_3 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 $ZT = \sigma S^2 T/k$ and power factor $PF = \sigma S^2$ where S is the Seebeck coefficient (V/K), σ is the electrical conductivity (S/m), k is the thermal conductivity (W/m K), and T is the absolute temperature in Kevin (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 [16] 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 [17], 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 1–5 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. The Bi_2Te_3 and Sb_2Te_3 thin films are grown by e-beam evaporation deposition, using a Kurt J. Lesker PVD 75 E-beam/thermal evaporation system. Solid antimony (III) telluride and bismuth (III) telluride (99.999% purity; Alfa Aesar Company) are evaporated for growth of the Bi_2Te_3 and Sb_2Te_3 thin films, respectively. The films are deposited at room temperature without substrate heating. The process chamber has a background pressure of 2×10^{-7} Torr. The thickness of Bi_2Te_3 and Sb_2Te_3 thin films is controlled by an INFICON deposition monitor during the deposition, and measured by Stylus Profilometry (Bruker, IL, USA). Table 1 summarizes all of the samples grown by e-beam evaporation and ion beam irradiation conditions.

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

The displacement energy is 25 eV for all of the elements in Bi_2Te_3 and Sb_2Te_3. The ion ranges of the 400 keV Ne^{2+} in thermoelectric thin films were 493 nm for Bi_2Te_3 and 520 nm for Sb_2Te_3, respectively, significantly larger than that of the film thickness (see Table 2). These results suggest that most of the implanted Ne^{2+} penetrated through the film thickness such that the chemical effort on the electrical and thermoelectric properties of the films

Table 1
Sample synthesis method, ion fluence and displacements per atoms (dpa) based on SRIM-2008 calculation.

Sample	Material	Condition	Ion fluence (10^{15} ions/cm^2)	dpa
N0	Bi_2Te_3	E beam	0	0
P0	Sb_2Te_3	E beam	0	0
N1	Bi_2Te_3	E beam + ion beam	0.5	0.09
N2	Bi_2Te_3	E beam + ion beam	1	0.19
N3	Bi_2Te_3	E beam + ion beam	5	0.93
N4	Bi_2Te_3	E beam + ion beam	10	1.87
P1	Sb_2Te_3	E beam + ion beam	0.5	0.07
P2	Sb_2Te_3	E beam + ion beam	1	0.15
P3	Sb_2Te_3	E beam + ion beam	5	0.74
P4	Sb_2Te_3	E beam + ion beam	10	1.49