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Interfacial mixing in Te/Bi thin film system

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ABSTRACT

100 MeV Ag ions have been used to study the swift heavy ion (SHI) induced modification in Te/Bi bilayer system. The samples were analysed using Rutherford backscattering spectroscopy (RBS), Atomic force microscopy (AFM) and X-ray diffractometer (XRD). The elemental depth study with RBS results show a strong mixing between the top Te layer and the underlying Bi layer on irradiation. Surface roughness as calculated by AFM is found to increase from 8 to 30 nm on irradiation for the fluence $3x10^{13}$ ions/cm^2. XRD results confirm the formation of Bi-Te alloy phases on mixing and are expected to be formed due to the interfacial reaction taking place within the molten ion tracks. Ion beam mixing has the potential to induce the formation Bi-Te alloy thin films which are the promising candidate for thermoelectric applications near room temperature. Copyright © 2014 VBRI press.

Keywords: Bismuth telluride; ion beam mixing; swift heavy ion; RBS; AFM; XRD.

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Introduction

Thermoelectricity is the generation of electricity due to an existing temperature gradient or vice versa and depends strongly on stoichiometric composition of the materials. For the rapid heat dissipation in certain electronic and microelectronic devices, high efficient thin film thermoelectric devices are essential. Bismuth telluride based alloy thin films are studied for their unique thermoelectric properties near room temperature **[1]**. It has been found that Bi-Te compounds under a stoichiometric ratio of 2:3 give best thermoelectric performance **[1, 2]**. Various researchers have tried to fabricate its thin films by thermal evaporation, chemical vapour deposition, pulse laser deposition, molecular beam epitaxy etc. However the light mass of Te and the wide variation in the vapour pressure of the constituent elements lead to the re-evaporation of Te from the surface developing anti-site defects where excess Bi (Te) takes the position of the Te (Bi) lattice **[3].** Approaches were made by inducing interfacial reaction between Bi/Te layers by post annealing of Bi/Te multilayer [4]. Co-evaporation of pure Bi and Te was used so as to have independent control of the deposition parameters **[5].** Here we will deal with the ion beam mixing of Te/Bi due to the SHI which dissipate energy mainly through the electronic energy deposition. For very small film thickness, the electronic energy loss value (S_e) will remain almost constant throughout the film and there is possibility for the entire film to get mixed. Energetic ions like SHI play a major role in synthesis, material modifications and characterisations. Material modifications include ion beam mixing where atoms of one layer mingled with the atoms of other layers under the influence of energy deposited by the incident ions.

Two theoretical models viz. Coulomb explosion model **[6]** and thermal spike model **[7]** are proposed to explain the electronic energy loss mechanism. Thermal spike model has successfully explained the ion beam mixing process both in metals and non-metals. Several researchers have demonstrated that SHI induced mixing in the interface takes place as a consequence of interdiffusion during the transient melt phase **[8, 9**]. It was shown that the diffusivity of the ions across the interface during the transient melt phase is about 10^{-6}-10^{-9} m^2/s. Such a high value of diffusivity is feasible only for liquids, thus supports that ion beam mixing is due to interdiffusion of the atomic layers during the transient melt phase. Wang et al. **[10]** has shown that SHI can induce a molten phase both in Ni/Ti interface when bulk Ni is S_e insensitive for a value below 67 keV/nm **[11]** and Ti is sensitive leading to intermixing. Kraft et al. **[8]** and Schattat et al. **[12]** studied mixing in ZnO/SiO_2 and CuO_x/SiO_2 respectively as a function of the electronic stopping power (S_e). A threshold value S_{th} was reported to exist below which mixing ceases to occur while above which mixing increases with increasing (S_e). However it has also been reported that mixing occurs well below the threshold value in bulk form **[13].** For a threshold of 24keV/nm in Bi (bulk), a damage induced by electronic slowing down was reported by Dufour et al. **[14]**. S_e sensitivity of Te is not known. To the best of our knowledge there is no study reported on swift heavy ion beam induced mixing on Te/Bi system. Few reports are available on ion beam mixing in Bi/Te bilayer system using low energy Kr ions **[15]**. Thus in the view of properties of the material sensitivity towards swift heavy ion, Te/Bi system is studied.

In this work, swift heavy ions have been used to induce mixing in Te/Bi system and lead the possibility of formation of technologically important materials in thin film forms. Ion beam mixing technique for thin film preparation has been known to control the stoichiometry of the mixed layer by regulating ions per atom arrival ratios **[16]**. Thus with appropriate ion beam parameters, one can control and regulate the stoichiometry of the desired alloy formed. It has the advantage of selective and localised area of material modifications.

Experimental

The Te (~150 nm)/Bi (~150 nm) thin films were prepared by successive thermal evaporation of Bi and Te respectively over cleaned glass substrate under the pressure 10^{-5} torr at room temperature. The glass substrates were cleaned in warm freshly prepared chromic acid and isopropyl alcohol each time rinsed in distilled water. High purity Bi (Koch-Light, 99.999%) and Te (Aldrich, 99.999%) were taken as evaporants in Mo boat. The bilayer was irradiated with 100 MeV Ag^{+7} ions with beam current of 1 pnA under a varying fluence of 10^{12} – 10^{14} ions/cm^2 delivered by 15 UD pelletron facility at Inter-University Accelerator Centre (IUAC), New Delhi. The irradiation was carried out at room temperature and pressure maintained was 10^{-6} torr. For uniform irradiation, the focussed beam was allowed to scan over an area of 1 x 1 cm^2. The stopping powers (S_e and S_n) and range of 100 MeV Ag ions in Bi and Te layer as calculated by Stopping range of ions in matter (SRIM) program **[17]** are given in the **Table 1**.

Table 1. The calculated electronic energy loss (S_e) and nuclear energy loss (S_n) values of 100 MeV Ag ions on Bi and Te target using SRIM simulation code.

Samples	**100 MeV Ag ions**		
	S_e (keV/nm)	**S_n (keV/nm)**	**Range (μm)**
Bi	17.1	0.1	10.3
Te	14.8	0.9	12.1

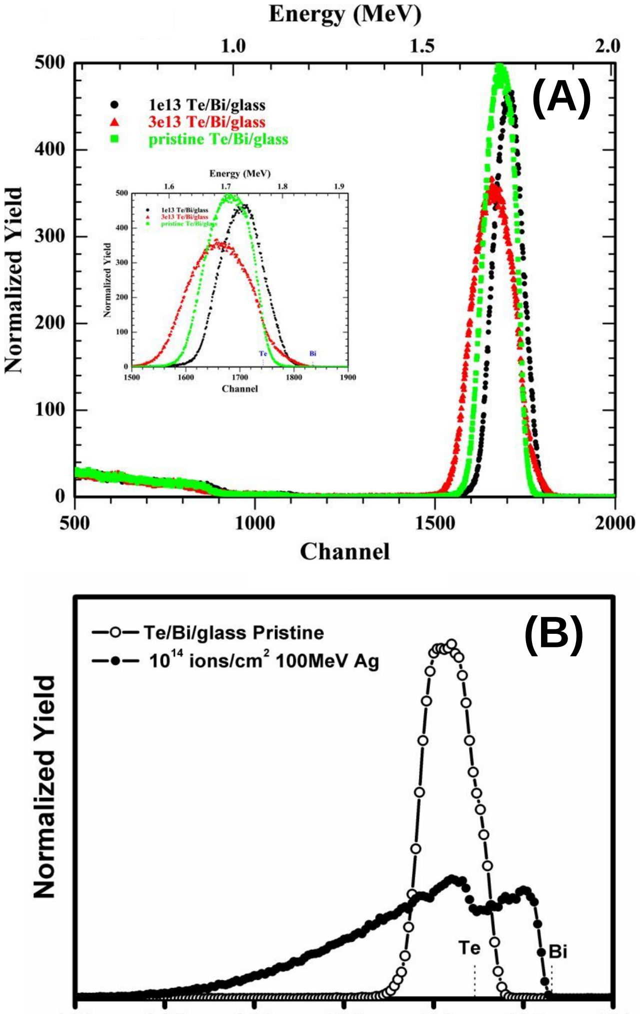

Fig. 1. (A) RBS spectra of pristine and 100 MeV Ag ions irradiated samples of Te/Bi over substrate using 2.0 MeV He ions under the fluences $1x10^{13}$ and $3x10^{13}$ions/cm^2. Inset shows the selected region of spectra comprising the Te/Bi layers. The simulated positions of energies of He-particles scattered from the surface atoms of Bi and Te are given and **(B)** Energy spectra of 2.4 MeV He ions backscattered from Te/Bi bilayer system on and before irradiation with 100 MeV Ag^{+7} ions. The hollow and the black circles represent the pristine and irradiated samples respectively.

The pristine and irradiated samples were characterized by RBS, AFM and XRD. The elemental depth study was done with RBS using 2.4 MeV He^{+2} ions and current of 30 nA for the pristine and 100 MeV Ag^{+7} ions irradiated samples under the fluence 10^{14} ions/cm^2 in CSNSM, Orsay, France. The RBS of the lower fluences 10^{13} and $3x10^{13}$ were done using the 1.7 MV RBS facility at IUAC, New Delhi. The data were analysed using Rutherford Universal Simulation Program (RUMP) **[18, 19]**. Surface morphology was studied using Digital Instrument Nanoscope IIIa in IUAC, New Delhi at room temperature under tapping mode. Roughness on and before irradiation were compared as tailing in the RBS spectra may be either due to roughness of the surface or layer interpenetration taking place between layers. XRD was carried out with CuKα radiation from Bruker D8 X-ray diffractometer in the 2θ scan region of 20-55^0 at a glancing angle of 2^0 with scan speed 0.5^0/min in IUAC, New Delhi.

Results and discussion

Interface mixing

Fig. 1(A) shows the RBS spectra of the pristine and irradiated Te/Bi samples as a function of fluence analysed using RUMP simulation code. The RBS spectra of the pristine sample comprise of single narrow signal peak. The presence of Te on the top gives underlying Bi signal a lateral shift towards lower energy which ultimately merges with Te signal peak. The pristine sample gives a thin intermixed layer of Bi and Te in between Te layer and oxide of Bi layer. On irradiation with 100 MeV Ag ions, the peak gets broadened owing to the shifting of the edges along the lower and higher energy edges. It may be explained as the underlying Bi layer extends up to the top surface layer while top lying Te atoms buried deeper into the Bi layer due to the interdiffusion taking place within the system. Fluences of $1x10^{13}$ions/cm^2 witness the entrance of Bi at the top surface while $3x10^{13}$ions/cm^2 shows the appearance of roughness and diffusion at both sides. Increase of FWHM shows the diffusion taking place into the glass substrate. The broadening of the spectra and shifting of the edge towards higher energy show efficient mixing place within the system **[20]**. It can be observed that interdiffusion across the interface takes place resulting in the existence of underlying Bi on the top surface with Te diffused within the layer. On further increasing the fluence to $1x10^{14}$ions/cm^2 as shown in **Fig. 1(B),** a strong tailing at the lower edge is observed showing the diffusion of both the elements into the glass substrate at the same rate. Thus higher fluences lead to the interdiffusion of the Te/Bi thin film system into the substrate.

The spectra were fitted and the constituting depth profiles were extracted using the RUMP simulation code as shown in **Fig. 2(A-C).** Pristine sample comprises of 130 nm Te layer followed by 40 nm of interdiffused layer of Te-Bi and Bi oxide layer. Bi thin film reacted with atmospheric oxygen during the breakage of vacuum while loading Te sample for the following deposition leaving aside 15 nm of pure Bi layer. Moreover the evaporation was carried out at 10^{-5} torr leading to the presence of residual oxygen inside the chamber which might have reacted with the freshly prepared Bi thin film. A small fraction (less than 10%) of Bi has been found to diffuse into the glass substrate for a depth of 120 nm. On irradiation with 100 MeV Ag ions under the fluence 10^{13} ions/cm^2, interdiffusion of Bi and Te increases leaving aside 70 nm Te layer and 90 nm of Bismuth oxide layer. Expulsion of oxygen due to phase separation during swift heavy ion is also been reported by Srasthi et al **[21]**. Similarly as we increase the fluence to $3x10^{13}$ ions/cm^2 diffusion across the interface increases further leading to the appearance of Bi on the top surface and Te in the bottom of the bilayer. Bi diffusion towards the substrate remains the same for the lower fluence but increases with the fluence.

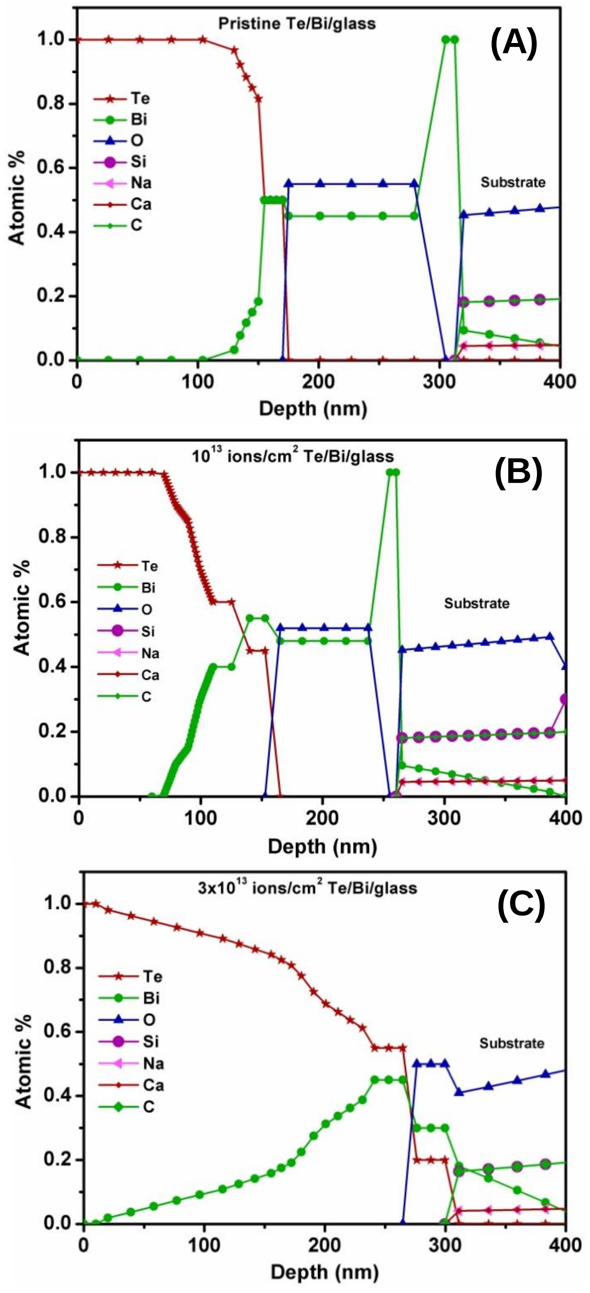

Fig. 2. Atomic composition with respect to depth as extracted from RBS simulation fit (A) Pristine Te/Bi over glass substrate and 100 MeV irradiated Te/Bi under the fluence, **(B)** 10^{13} ions/cm^2 and **(C)** $3x10^{13}$ions/cm^2.

The broadening in the interface is contributed both by the surface roughness and intermixing **[22]**. The surface roughness is taken into account for the contribution towards the interdiffusion taking place. **Fig. 3(A-C)** represents the AFM images of the pristine and irradiated samples of Te/Bi thin film system.

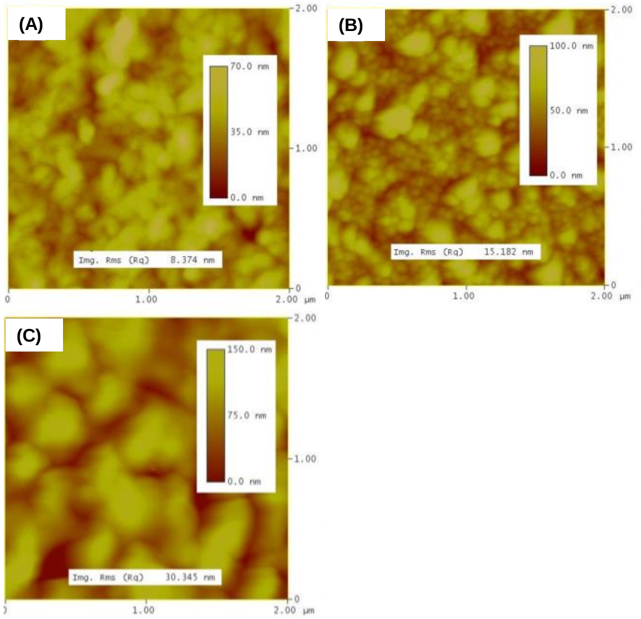

Fig . 3. AFM images of the (A) Te/Bi pristine sample over glass substrate and 100 MeV Ag ion irradiated Te/Bi sample for the fluence, (B) 10^{13} ions/cm^2 and (C) 3x10^{13} ions/cm^2.

The pristine sample gives a smooth surface with rms value of 8 nm and comprises of smaller grains. On irradiation with 100 MeV Ag ions, grains become coarse and have higher surface giving a rough surface. The effect is more pronounce as we go to higher fluences. Increase in the roughness is contributed by the larger grains due to phase formation as evidenced by the higher depth scale and sputtering of the surface layer. Thus roughness alone cannot account for the tailing in the RBS spectra.

Thermal spike calculation

Since the S_n values of Ag ions in Bi or Te layer are very small compared to S_e values, we account the interdiffusion process due to the electronic energy loss process of Ag ions within the layer. In order to understand the behaviour of the surface and interface of Te/Bi under the swift heavy ion irradiation, thermal spike model (TSM) calculation for the constituent layers is considered. TSM calculation is the theoretical prediction on the lattice temperature rise with time. According to which, the energy deposited in the electronic subsystem is transferred to the atomic subsystem via electron-phonon coupling. This results in a sudden rise of lattice temperature (thermal spike) up to 1000 K for a few picoseconds. During this transient temperature spike, the material within the ion path (nanometers) reaches molten state resulting in the interdiffusion of the comprising layers and hence mixing. Wang et al. **[10]** used thermal spike calculation to interpret mixing in the interface of Ni/Ti system. S_e sensitive Ti shows a maximum of 3500 K on irradiation with GeV Ta or U ions while the temperature rise is below the melting point in case of Ni. However Ni at the interface is melt due to the energy transferred from Ti lattice. Similarly Srivastava et al. **[9]** checked the hypothesis of transient molten state diffusion using the thermal spike model. Lattice temperature variation with time of Bi for 100 MeV Ag ions has been calculated using TSM. The physical parameters of Bi used for the calculation are electron-phonon coupling (g) 1.3 x 10^{11} Wcm^{-3}s^{-1} and thermal diffusivity 38 cm^{2}s^{-1} at 300 K **[23]**. However 'g' value for Te is not available due to lack of experimental results on this material and limit its lattice temperature variation calculation.

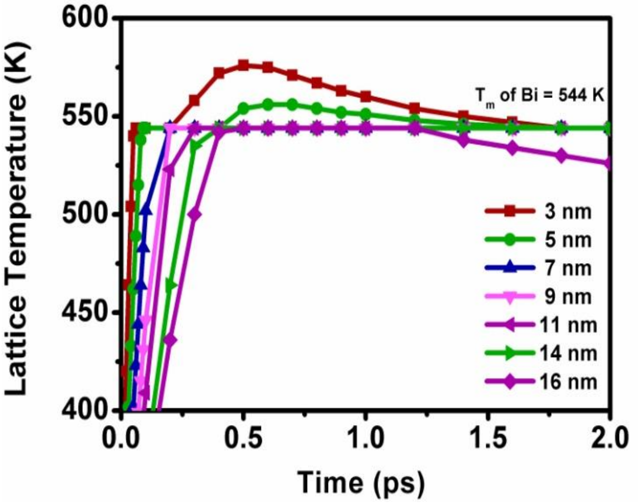

Fig. 4. Evolution of Bi lattice temperature versus time for various radii r around 100 MeV Ag ions as calculated using thermal spike calculation. The track radius is found to be around 6 nm. Here T_m denotes the melting temperature of Bi.

From the simulation result as shown in **Fig. 4.**, it is observed that Ag ions induce a molten phase in bulk Bi having a melting point of 544 K and the maximum lattice temperature attained is around 600 K. Track radius defined to be the radius of the ion track at which the lattice temperature just exceeds the melting point is around 6 nm for a duration of about 1 ps for 100 MeV Ag ions in Bi. However the lattice temperature increase in Bi is not sufficient to melt bulk Te having a melting temperature of 722 K. As evidence from the RBS results, mixing has been observed within the system on irradiation with SHI and it is well known that the melting point of thin films is lower relative to the melting point of its bulk counterparts **[24]**. Thus the rise in the lattice temperature of Bi could have raised the lattice temperature of Te in the interface to its melting point. Due to this heat generation in the lattice, both the layers in the interface reach its molten state leading to inter-diffusion during the transient melting phase.

Interfacial reaction

Interdiffusion on impact of swift heavy ion is observed in the present study. For the identification of the crystalline phases formed, the samples were examined by grazing incidence XRD. The XRD results are given in **Fig. 5** where the pristine sample mainly comprises of Te peak and few Bi_2O_3 and BiTe peaks. No peak of the elemental Bi is found since Bi appears to have reacted with the oxygen adsorbed on the surface of film or glass substrate **[25]**. The presence of BiTe phase in the pristine sample may be due to the mixing induced by high energetic atoms during the process of thermal deposition. On irradiation, Bi-Te alloy phases are identified at 2Ɵ values 27.54^0 and 40.39^0 while the elemental Te peak intensity either gets lowered or disappeared. Since the peak of Bi (2Ɵ = 27.26^0) and Te (2Ɵ = 27.70^0) are very close to each other, the peak at 2Ɵ = 27.54^0 is regarded to be the peak of Bi-Te alloy formed during the irradiation. It may be concluded that the interdiffusion across the interface is accompanied by interfacial reaction between the constituent elements. It is seen that Bi_2O_3 intensity also decreases remarkably after the irradiation.

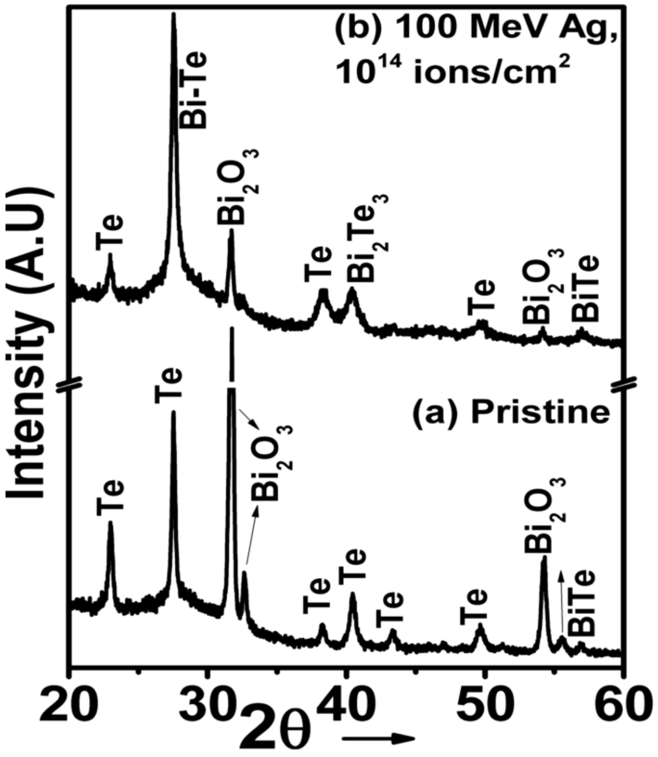

Fig. 5. X-ray diffraction pattern of (a) pristine Te/Bi samples and (b) on irradiation with 100 MeV Ag ions under the fluence 10^{14} ions/cm^2.

It should be noted that during SHI irradiation, within a fraction of picoseconds, certain point defects are formed and quenched to room temperature. The presence of these defects lowers the activation energy and hence enhances the mobility. This may lead to the formation of ordered phases even at lower than the eutectic temperature [**26, 27**]. For the mixed region comprising of Bi and Te, compound formation will take place while Te or Bi region will remain as such.

Conclusion

In conclusions, we have investigated swift heavy ion induced mixing in Te/Bi thin film system over glass substrate using 100 MeV Ag ions. We observed strong intermixing across the interface as a result of the energetic incident ions. The RBS results as analyzed with RUMP simulation code interpret the atomic diffusion between the comprising layers resulting in the broadening and spreading of the RBS spectra. Surface roughness as calculated by AFM is insignificant to contribute to the broadening and tailing of the RBS spectra. The XRD results have shown Bi-Te alloy phase formation on irradiation with swift heavy ion. Mixing can be concluded as a consequence of interdiffusion during the transient molten phase as estimated by thermal spike calculation. Thus, ion beams have been utilized to synthesis Bi-Te alloy thin films which form an important group of thermoelectric materials for application near room temperature.

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