Swift heavy ions having an equal electronic energy loss $S_e$ are utilized to induce interfacial mixing in Bi/Te bilayer system. The elemental depth analysis studied using RBS gives an unusual extent of mixing in the two cases. Sputtering yield derived from RBS and AFM results was found to be higher for ions moving with lower velocity. All these observations were attributed to the ion velocity effect.
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4.1 Introduction

In an ion – solid interaction, the slowing down of the incident energetic ion takes place via the collision with the target nuclei and the electronic system of the target material. This interaction not only depends on the type of the ions and target material but also on the ion velocity [1]. The nuclear energy deposition leads to the atomic displacement of the target atom and can be evaluated using the Monte Carlo simulation [2]. Interaction of swift heavy ion (SHI) with matter has become an important aspect due to a very large energy deposition in MeV range. With most of the energy being deposited via collision with electrons, this is considered to be in electronic stopping regime. This electronic stopping may lead to material modification, defect creation and defect annealing [3-5]. Waligorski et al [6] have discussed the radial distribution of energy deposited by the ions and can be fully described by an analytical equation which depends on the ion velocity. Studies on such energy distribution have been made on Y$_3$Fe$_5$O$_{12}$ [7-9] a magnetic insulator. For similar electronic loss value $S_e$ the irradiation gives track radii which increases as ion velocity decreases. The damage creation by the same electronic stopping value $S_e$ in Y$_3$Fe$_5$O$_{12}$ was strongly dependent on ion velocity. Dunlop et al [3, 10] studied the damage creation on metallic targets via electronic excitation and found to be dependent on ion velocities. Wang et al [11] reported the ion velocity effect on Bi target using Ar and Kr ions having $S_e$ values of 17 keV/nm. The results agreed well with the calculated and the experimental results of track radii with ion velocities. Similar effect was observed in the electronic sputtering yield in fullerene with Au and Ag ions [12].
In the present study, we have investigated the Bi/Te interface for the ion induced interdiffusion using the SHIs of Ag and Au of same $S_e$ value and studied the ion velocity effect by considering the extent of mixing in the two cases. The analysis was made with Rutherford backscattering spectroscopy (RBS) and Atomic force microscopy (AFM).

### 4.2 Experimental

A thin bilayer of Bi/Te of total thickness 165 nm was prepared over cleaned Si (100) substrate by thermal evaporation technique at room temperature. The Si substrate was cleaned with trichloro-ethylene solution followed by warm acetone or alcohol solution. The pressure was made sure not to drop below $10^{-5}$ mbar during the deposition. For ion irradiation, Au and Ag ions with energy value having same $S_e$ values were chosen for irradiation. Irradiations were carried out with 90 MeV Au$^{+8}$ and 95 MeV Ag$^{+7}$ ions with fluences $1 \times 10^{12}$, $3 \times 10^{12}$, $1 \times 10^{13}$, $3 \times 10^{13}$ and $6 \times 10^{13}$ ions/cm$^2$ using the 15 UD tandem accelerator in Inter University Accelerator Centre (IUAC), New Delhi. The vacuum in the chamber was maintained at $10^{-6}$ mbar and ion current was 1.5 pnA. With such high energy heavy ions, the electronic stopping power ($S_e$) is of the order of several keV/nm (as shown in Table 4.1) and can be considered to be constant in each component of the bilayers. The ratios between the electronic and nuclear stopping powers are about tenth to hundredth so that the experimental results could be considered due to electronic excitation effects.
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Table 4.1. The calculated electronic energy loss ($S_e$) and nuclear energy loss ($S_n$) values of 90 MeV Au and 95 MeV Ag ions on Bi and Te target using SRIM [1] simulation code

<table>
<thead>
<tr>
<th>Target</th>
<th>Incident ion</th>
<th>Energy (MeV)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>Ag</td>
<td>95</td>
<td>16.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Bi</td>
<td>Au</td>
<td>90</td>
<td>16.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Te</td>
<td>Ag</td>
<td>95</td>
<td>14.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Te</td>
<td>Au</td>
<td>90</td>
<td>14.7</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The pristine and irradiated samples of Bi/Te were studied using 1.7 MV RBS facility in IUAC recording the backscattered spectra of 2.00 MeV He$^+$ ions. The RBS data were used to derive the elemental depth profiles of the samples using the RUMP simulation code [13, 14]. Surface morphology and topography of the samples were studied with AFM model Digital Nanoscope IIIa under the tapping mode.

4.3 Results and discussions

4.3.1 RBS: Depth analysis

Figure 4.1 shows the recorded spectra of the backscattered He$^{+2}$ ions for the pristine and irradiated samples of Bi/Te bilayer system. The signals from Bi and Te are separated with the higher signal peak corresponds to Bi and lower signal peak is to Te. Only the RBS spectra of maximum fluence $6\times10^{13}$ ions/cm$^2$ are discussed since lower fluences were of less significance. The pristine sample shows a slight merging of the lower energy edge of Bi and higher energy edge of Te revealing interdiffusion of the atomic layers during deposition process. On irradiation with 95 Mev Ag ions, the merging of the edges in the interface increases and the slope
of the lower edge of Bi and higher edge of Te peak decreases. This signifies mixing in the Bi/Te interface. The merging of the edges is more pronounced for 90 MeV Au ions irradiation. The relative RBS yield of the respective elements decreases on irradiation. The broadening of the RBS spectra and lowering of the interfacial slope clearly indicate interdiffusion taking place due to the energy imparted by the SHIs [15]. It is observed that Bi and Te seem to have reacted thermally at the room temperature which is enhanced by SHI irradiation.
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Fig. 4.1 Backscattering spectra for 2.00 MeV He$^{+2}$ ions incident on 165 nm thick Bi/Te thin film on Si substrate (a) for a channel of 1000 – 2000 showing the substrate and (b) for a channel of 1600 - 2000 showing the interface of the Bi and Te signals. The pristine sample is represented by (■), 90 MeV Au and 95 MeV Ag ions irradiated sample by (▲) and (*) respectively for the fluence $6 \times 10^{13}$ ions/cm$^2$. 
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The fitted spectra and corresponding concentration profiles as extracted from the RUMP simulation are shown in the Figure 4.2. The pristine sample of Bi/Te layer extends upto 165 nm of the depth. Top layer comprises of a few nm of bismuth oxide owing to the reaction of freshly prepared Bi/Te thin film on exposure to atmosphere. In the following layers, Te is linearly diffused to a percentage of 0.1-55% into Bi layer while Bi is diffused up to 1–45% into Te layer which is expected to be formed due to the mixing induced by the implanted species having high kinetic energy during the deposition process [16]. 35 nm thick Te layer is present in the pristine sample over the Si substrate.

On irradiation with 95 MeV Ag ions for a fluence of $6 \times 10^{13}$ ions/cm$^2$, the diffusion of both the constituents across the interface increases with a linear diffusion of 45-60% for Te into Bi (~58 nm), 30-40% Bi into Te (~20 nm) and 1-30% Bi into Te (~40 nm). A thickness of 22 nm elemental Te layer still remains intact with Si substrate and small fraction diffusion into the Si substrate. For irradiation with 90 MeV Au ions with fluence $6 \times 10^{13}$ ions/cm$^2$, the diffusion increases as can be witnessed from the increase in the thickness of the mixed layer and consumption of the whole Te layer. The depth of Te diffusion into the substrate extends up to 85 nm compared to 65 nm in Ag ion irradiation with diffusion percentage remaining almost the same. Further the depth of Bi extends up to 126 nm as compared to 118 nm in Ag ion irradiation.
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Fig. 4.2 RBS simulation fit for Bi/Te/Si and the respective depth profile extracted using RUMP simulation code for (a) pristine sample, (b) 95 MeV Ag irradiated and (c) 90 MeV Au irradiated at the fluence $6 \times 10^{13}$ ions/cm$^2$. 
4.3.2 Sputtering yield

From the depth analysis of the Bi/Te pristine and irradiated samples, the total thickness of Bi/Te layer decreases significantly on irradiation. The total thickness of the Bi/Te layer in the pristine sample is estimated to be 165 nm which decreases to 125 nm and 118 nm respectively for Ag and Au ions irradiation. The integral of the Bi signal also decreases considerably on irradiation. Ion beam mixing is known to be associated with the sputtering of the film surface [17, 18]. Thus we can assume a few nanometres of the top surface to be sputtered away on impact of the heavy ion which account for the decrease in the thickness and the integral of Bi signal peak.

To calculate the sputtering yield

\[
Areal\ concentration, N_t = \frac{Y \times \sin \alpha}{N_p \times \frac{d\Omega}{d\sigma} \Omega}
\]  
(4.1)

Where \(Y\) = area under the RBS curve

\(\alpha\) is taken as 90\(^0\)

\(\Omega\) is the solid angle obtained from RBS data (= 5x10\(^{-13}\) Sr)

\(\frac{d\Omega}{d\sigma}\) is the cross section

\(N_p\) = no of incident ions = \(\frac{\text{total charge } C}{\text{charge state } \times 1.6 \times 10^{-19}}\)  
(4.2)

For a fluence i.e. 6x10\(^{13}\) ions/cm\(^2\),

\[
Sputtering\ yield = \frac{N_{fluence} - N_{pristine}}{fluence}
\]  
(4.3)
The sputtering yield of Bi due to Ag- and Au- ions for the fluence $6 \times 10^{13}$ ions/cm$^2$ calculated is found to be 173 and 206 atoms per ion respectively. A similar sputtering yield of 200 for Bi on irradiation with 120 MeV Au ion has been reported [19].

**4.3.3 AFM: Surface roughness**

Irradiation leads to the broadening of the interfacial edges of the Bi and Te distribution since the edges of the RBS spectra become less steep. It should be noted that broadening obtained from RBS, $\sigma_{\text{RBS}}^2$ is composed of the variance of the interfacial concentration gradient $\sigma_{\text{mix}}^2$ and the lateral fluctuation of the surface layer thickness $\sigma_d^2$, which itself contains both the interface and surface roughness [20]. Thus $\sigma_{\text{RBS}}^2$ gives the influence of the surface roughness on and the variance observed for the Bi/Te interface. It may be concluded that broadening is caused by atomic mixing of the interface and roughening of the surface due to the sputtering. The relative changes in the variances $\Delta \sigma_{\text{RBS}}^2 = \sigma_{\text{RBS}}^2(\Phi) - \sigma_{\text{RBS}}^2(0)$ are calculated for the fluence $\Phi = 6 \times 10^{13}$ ions/cm$^2$ and the pristine sample. Thus the difference $\Delta \sigma_{\text{RBS}}^2 - \Delta \sigma_{\text{AFM}}^2$ can be regarded as the direct measure of the interface mixing effect.

In order to obtain surface roughness, the system was investigated with AFM. Figure 4.3 shows the AFM images of Bi/Te over Si substrate in two dimensions and three dimensions at the 2 µm scale. The pristine surface comprises of highly oriented uniform grains and is rather smooth with an rms value of 7 nm. On irradiation with SHIs, the surface becomes higher as evidenced from the depth scales and grains seem to grow larger giving an rms value of 21 and 26 nm for 95 MeV Ag and 90 MeV Au ions respectively. The triple fold increase in the
roughness may be due to combine effect of structure formation leading to increase in grain growth and surface sputtering.

Fig. 4.3 Surface topography of Bi/Te/Si measured by AFM (tapping mode) in 2D and 3D (a) pristine sample, (b) 95 MeV Ag ion and (c) 90 MeV Au ion irradiated under the fluence 6x10^{13} ions/cm^2.
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For a bilayer sample, the concentration profiles can be described by a Gaussian error function, the change \( \Delta \sigma^2(\Phi) = \sigma^2(\Phi) - \sigma^2(0) \) of their variances \( \Phi^2 \) due to the irradiation is taken as a measure of the mixing effect [21] where \( \sigma^2(\Phi) \) and \( \sigma^2(0) \) are the variances of the irradiated and pristine samples respectively and \( \Phi \) is the fluence. The calculated mixing variance as obtained from the above relation is given in the Table 4.2.

Table 4.2. Energy, ion, mixing variance from RBS, AFM and due to interface mixing for Bi/Te thin film system

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Ion</th>
<th>( \Delta \sigma_{\text{RBS}}^2(\Phi) ) (nm²)</th>
<th>( \Delta \sigma_{\text{AFM}}^2 ) (nm²)</th>
<th>( \Delta \sigma_{\text{RBS}}^2(\Phi) - \Delta \sigma_{\text{AFM}}^2 ) (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>Ag</td>
<td>882</td>
<td>449</td>
<td>433</td>
</tr>
<tr>
<td>90</td>
<td>Au</td>
<td>1833</td>
<td>728</td>
<td>1005</td>
</tr>
</tbody>
</table>

Table 4.2 shows the mixing variance at the interface of Bi/Te which is higher for Au irradiated samples. We had expected a same degree of mixing in both the cases since these have same \( S_e \) values. However the slower 90 MeV Au ions have greater impact on interfacial mixing and sputtering yield than the faster 95 MeV Ag ions. Neglecting the contribution of the nuclear stopping power \( S_n \) to the total mixing effect as its values were rather small compared to \( S_e \) values, we speculate the variation as due to the ion velocity effect of ions in Bi/Te system. SHIs are known to have radial distribution of deposited energy as studied by Waligorski et al. [6] and it depends on the ion velocity. Damage creation by electronic excitations is governed by the recoil energy, \( E_r \) which is characterized by a parameter \( \eta \). The space charge created along the ion path varies with \( \eta \propto \left( \frac{Z_1^*}{v} \right)^2 \) where \( v \) is the ion velocity and \( Z_1^*(v) \) is the ion effective charge deduced from
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Northcliffe formula [22]. Introducing a dimensionless parameter \( \eta = \frac{Z_1 v_0}{v} \), \( v_0 \) is the Bohr velocity the electric field resulting from the space charge varies with \( \eta^2 \). Thus, the parameter \( \eta \) increases monotonically as the ion slows down and gives a variation in the damage creation or track formation. Hence the pertinent parameter characterizing the part of the energy deposited in the electronic excitation which is converted to atomic movements is \( \eta = \frac{Z_1 v_0}{v} \) [10]. For a surface or an interface between two materials, the cylindrical geometry along the ion trajectory does not hold any longer. The electrical field and thus the atomic impulses have non-vanishing components perpendicularly to the interface, which favour inter-atomic mixing at interfaces [23] or sputtering at free surface. For the same electronic energy deposition (\( S_e \)) the energy density around a slower ion is higher compared to the faster moving ion. Inspite of having same \( S_e \) values, Au ion was calculated to be 1.3 times slower to Ag ion. This slower ion should have produced higher density of defects around the ion trajectory or track radii leading to a higher extent of interdiffusion and higher sputtering of Bi layer. Pure Bi has been found to show ion velocity effect and the result was interpreted using thermal spike model where latent track radii were estimated w.r.t time [11].

4.4 Conclusions

In conclusion, SHIs of Au and Ag having same \( S_e \) values can be used to induce intermixing in Bi/Te thin film system. Mixing can be regarded as a consequence of the electronic energy deposition since nuclear energy deposition is
negligible. The mixing variance and sputtering yield due to 90 MeV Au ions were higher compared to those of 95 MeV Ag ions. These have been accounted to the ion velocity effect of the slower Au ions which is 1.3 times slower to Ag ions. Thus we come to the conclusion that not only Bi but Bi/Te system also shows ion velocity effect on ion beam mixing.
REFERENCES


