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Role of Heat of Mixing in Swift Heavy Ion Induced Effects

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Abstract—*In the present work, we have investigated the role of heat of mixing (HOM) in miscible metal/semiconductor systems. Swift Heavy Ions (SHI) with high energy of the order of MeV creates extensive defects along the ion path hence used for the modification at the interface of the sample. We have used Au ions with energy 120 MeV for irradiation of the samples at different fluences from 1×10^{13} to 1×10^{14} ions/cm^2. We have made three types of samples by taking three different metals Zirconium, Niobium, and Vanadium separately with the semiconductor Germanium for making the samples. For the characterization of the irradiated samples we used Rutherford Backscattering Spectroscopy (RBS) for the depth profile, Atomic Force Microscopy (AFM) for surface roughness and Grazing Incidence X-ray Diffraction (GIXRD) for phase identification. We have calculated the mixing rate, mixing efficiency and inter-diffusion coefficient for all the systems. We observed that interface mixing increases with the magnitude of negative heat of mixing.*

1. INTRODUCTION

The knowledge of basic ion-solid interaction phenomena has contributed greatly to materials science. The basic difference of materials modification by low energy ion implantation and high energy ion irradiation is that the low energy ions get embedded in the material and cause modification by their presence and due to the collision cascade produced by the impinging ions, whereas in high energy ion irradiation, the modification of thin films or the near-surface region of the bulk samples is due to the electronic excitation of the atoms in the materials. Swift heavy ions (SHI), having velocity comparable to the velocity of orbital electrons, cause exotic effects in different classes of materials which otherwise cannot be generated by any other methods. SHI irradiation of solids leads to materials modification such as micro structural changes, interface modification, or creation of new phases [1]. Interface modifications include ion beam mixing where atoms of one layer mingled with the atoms of other layer under the influence of energy deposited by the incident ions. For very small film thickness, the electronic energy loss value (S_e) will remain almost constant throughout the film. Ion beam effect on the materials depends on the ion energy, fluence and ion species. In most cases, materials modification by SHI irradiation exhibits a threshold value of electronic energy loss (S_e) beyond which the defect production efficiency increases to a great extent [2]. According to thermal spike model [2], during the passage of SHI, the kinetic energy of the ejected electrons is transmitted to the lattice by electron–phonon interaction, resulting in the increase of local lattice temperature above the melting point of the material. The temperature increase is followed by a rapid quenching, which results in an amorphous columnar structure when the melt solidifies.

Transition metal silicides have technological applications as contact materials, gate electrodes or interconnect materials in microelectronic devices. Ion beam mixing has been studied for different metal/silicon systems using SHI irradiation [3-7]. The reports on metal germanides have opened up exciting possibilities of using them as low resistive contact materials in very large scale integration technology. Low electrical resistivity offered by metal germanides, make them potentially better candidates for use as contact and interconnect materials than the well-known metal silicides [8]. Germanides are potentially valuable for making new alloys with special physical properties. The germanides of alkaline and alkaline earth metals are semiconductors and those of the transition metals have metallic properties. The germanides of niobium and vanadium and of vanadium-based alloys, which become superconductors at relatively high temperatures (Nb_3Ge, 6.3 K; V_3Ge, 6.01 K), are of great interest.

The formation of oriented $Au_{0:6}Ge_{0:4}$ alloy was observed when Au/Ge bilayer structure on Si was irradiated using 120 MeV Au ions and subsequently vacuum-annealed at 360^0C followed by natural cooling [9]. Ni_2Ge alloy phase formation due to 100 MeV Au-ion irradiation for ion fluence of 1×10^{14} ions/cm^2 was reported [10]. At Cu/Ge interface, it was found that, the mixing increases with the fluence, with the electronic energy loss and with the irradiation temperature [11]. Our previous study of Bi/Ge system shows strong mixing at the interface due to SHI irradiation [12]. In the present work, we have taken metals niobium, zirconium and vanadium separately with the semiconductor germanium and tried to find out the mixing effect when irradiated with 120 MeV Au ions at room

temperature at the fluences from 1×10^{13} ions/cm^2 to 1×10^{14} ions/cm^2. These systems have been characterized using Rutherford backscattering spectroscopy (RBS) for depth profile analysis, grazing incidence X-ray diffraction (GIXRD) for phase determination and atomic force microscopy (AFM) for surface roughness.

2. EXPERIMENT

For our experiment, thin films of metal and semiconductor were deposited on silicon [100] substrate by electron beam evaporation in the UHV deposition system. This was a cryo-pumped system equipped with a four-pocket electron gun in the target lab at Inter University Accelerator Center, New Delhi. First the substrates of 1cm x 1cm were obtained from a Si wafer. These were sequentially cleaned using trichloroethylene, acetone and alcohol. Finally, these were washed with de-ionized water before being transferred to the evaporator. Ge of 50 nm thickness was deposited on this Si substrate. Then Zr of 50 nm thickness was deposited on to the Ge layer. Finally carbon of 10 nm thickness was deposited as the top layer to avoid the oxidation. The thickness of the deposited layers was monitored using quartz crystal during deposition. The deposition of all the three layers Ge/Zr/C was performed at room temperature without breaking the vacuum to minimize impurities at the interface. Similarly Ge (50 nm) / Nb (50 nm) / C (10 nm) and V (50 nm) / Ge (50 nm) / C (10 nm) layers were deposited on the silicon substrate in UHV deposition system. The vacuum during deposition was ~ 3×10^{-6} - 4×10^{-8} Torr. Thin 10 nm layer of C was given on top of all the samples to avoid oxidation. We have deposited Si/Ge/Zr/C, Si/Ge/Nb/C and Si/V/Ge/C samples.

These samples have been irradiated with 120 MeV Au ions with fluence of 1×10^{13}, 5×10^{13} and 1×10^{14} ions/cm^2 using 15 UD Pelletron at IUAC, New Delhi. For irradiation, the samples were mounted on a copper ladder with a good thermal contact using a thermally conducting adhesive, so that the increase in the sample temperature during irradiation is negligible. The samples were irradiated uniformly at room temperature over an area of 1cm × 1cm by scanning the ion beam using an electromagnet scanner. Flux was kept low ($<10^{10}$ ions cm^{-2} s^{-1}) to avoid sample heating due to irradiation. The pressure in the irradiation chamber was $\sim10^{-6}$ Torr. The irradiation fluence was estimated by using the formula, fluence = (6.25×10^9 × time × current) / (area × charge state).

The electronic and nuclear stopping power for Zr, Nb and V using 120 MeV Au ions for irradiation are given in table 1, as calculated using simulation program SRIM [13]. The characterization of all the samples before and after irradiation was done using Rutherford backscattering spectrometry (RBS) for depth profiles and composition and phase identification using GIXRD at IUAC, New Delhi. The RBS experiments were performed using 2 MeV He ions with scattering angle of 167^0. The roughness of the top layer of pristine and irradiated samples was determined by atomic force microscopy (AFM) using a Nanoscope IIIa scanning probe microscope in the tapping AFM mode at IUAC, New Delhi. The scanned area was of 2μm × 2μm. This study helped us to make sure that the observed broadening in the RBS spectra is not due to surface roughness but because of interface mixing.

3. RESULTS AND DISCUSSION

Fig. 1, 2 and 3 shows the RBS spectra of pristine and irradiated samples of Si/Ge/Zr/C, Si/Ge/Nb/C and Si/V/Ge/C respectively as a function of fluence.

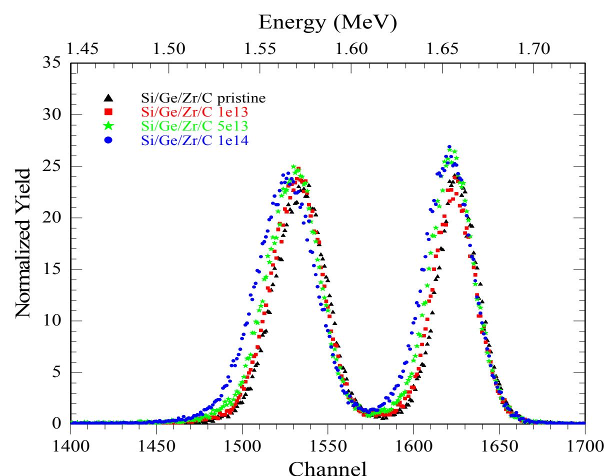


Fig. 1: RBS spectra of Si/Ge/Zr/C samples (pristine and irradiated).

The RBS spectra were fitted and the depth profiles were extracted using the RUMP simulation code. On irradiation with 120 MeV Au ions, the broadening of Ge and metal (Zr, Nb and V) peaks are observed which increases with increasing fluence. Broadening of the peak is maximum for Zr/Ge system in comparison to Nb/Ge and V/Ge systems. The variance was calculated from the spectrum height at 16% and 84%.

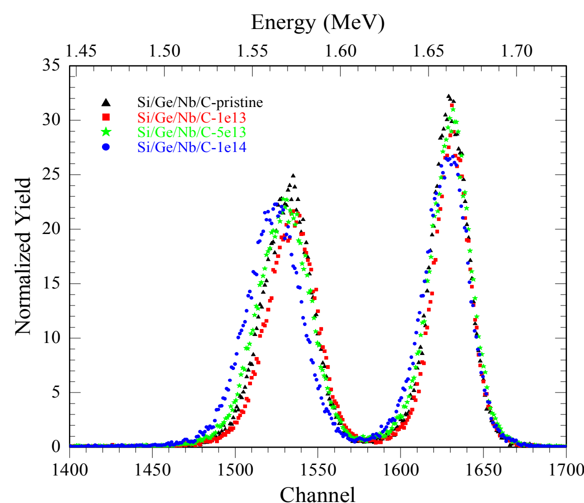


Fig. 2: RBS spectra of Si/Ge/Nb/C samples (pristine and irradiated).

Since the surface roughness was very small compared with the thickness of the mixed region, it was neglected while calculating the variance of the mixed region.

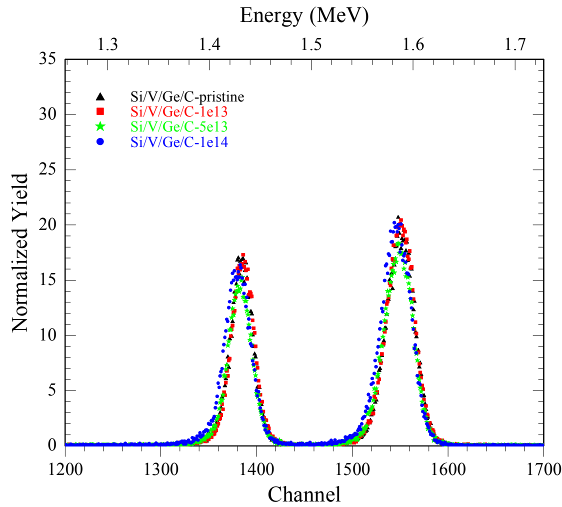


Fig. 3: RBS spectra of Si/V/Ge/C samples (pristine and irradiated).

The increase of the variance $\Delta\sigma^2(\phi) = \sigma^2(\phi) - \sigma^2(0)$ (where $\sigma^2(\phi)$ and $\sigma^2(0)$ are the variance of irradiated and as-deposited samples and ϕ is fluence) was calculated. The mixing rate defined as $k = \Delta\sigma^2(\phi)/\phi$ quantifies the mixing effect for the Metal/Germanium systems under irradiation with 120 MeV Au ions. The linear relationship between the interface broadening $\Delta\sigma^2(\phi)$ and the applied ion fluence ϕ is illustrated in Fig. 4. The mixing rates and mixing efficiency (k/S_e), obtained for the different systems are given in table 1. The mixing rate in the case of Nb/Ge is low in comparison to Zr/Ge system at the same energy.

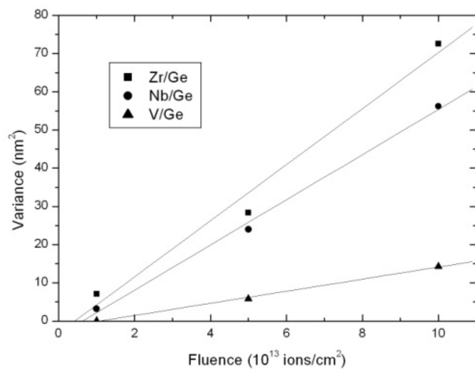


Fig.4 Plot of Varience Vs Fluence for Zr/Ge, Nb/Ge and V/Ge samples.

Both the Zr [2] and a-Ge [10] are S_e sensitive materials, therefore higher mixing is expected in this case as compared to Nb/Ge where Nb [2] is insensitive to S_e. It has been experimentally observed according to the expectation. The mixing rate in V/Ge system is low though Vanadium [2] is sensitive to electronic energy loss. This can be attributed to low heat of mixing in V/Ge in comparison to Nb/Ge and Zr/Ge given in table 2. All the samples Zr/Ge, Nb/Ge and V/Ge have negative heat of mixing. Fig.5 shows the plots of HOM with atomic concentrations of Metal/Germanium.

Table 1: S_e values of materials, mixing rate and mixing efficiency.

Energy (MeV)	Ion	Sam-ple	S_e (keV /nm)	Mixing rate k (nm^4)	Mixing efficiency (nm^5/keV)
120 MeV	Au	Zr/Ge	24.36 /19.5	73.3± 1.49	3.009
		Nb/Ge	31.95 /19.5	59 ± 3.58	1.84
		V/ Ge	27.78/19.5	15.8± 0.71	0.568

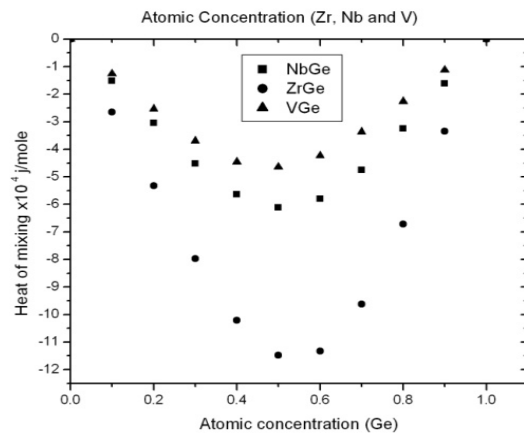


Fig. 5: Heat of Mixing with concentration of Metal/Germanium.

The roughness of the top layer of the pristine and irradiated with fluence (1×10^{14} ions/cm^2) for all the three samples are determined by AFM. Fig. 6,7and 8 shows the AFM patterns of Zr/Ge, Nb/Ge and V/Ge samples respectively for pristine and Au ions irradiated with fluence 1×10^{14} ions/cm^2. The root mean square values for different samples pristine and irradiated are shown in table 3.

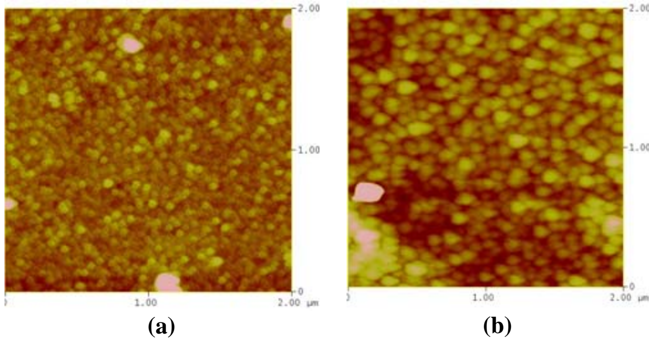
Table 2: Comparison of mixing rate, Se sensitivity and heat of mixing

		Zr/a-Ge	Nb/a-Ge	V/a-Ge
(i)	Mixing rate	Zr/Ge > Nb/Ge > V/Ge		
(ii)	Sensitivity to S_e	Yes/Yes	No/Yes	Yes/Yes
(iii)	Heat of mixing	Negative	Negative	Negative
		|HOM of Zr/Ge| > |HOM of Nb/Ge| > |HOM of V/Ge|		

Table 3: Root mean square value using AFM

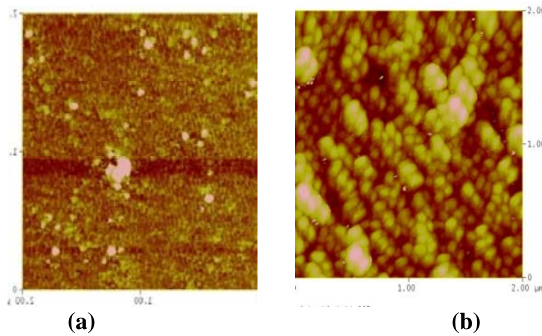
Samples	Pristine	Fluence (1×1014 ions/cm^2)
Ge/Zr/C	0.718 nm	3.006 nm

Ge/Nb/C	1.274 nm	7.406 nm
V/Ge/C	1.954 nm	4.155 nm



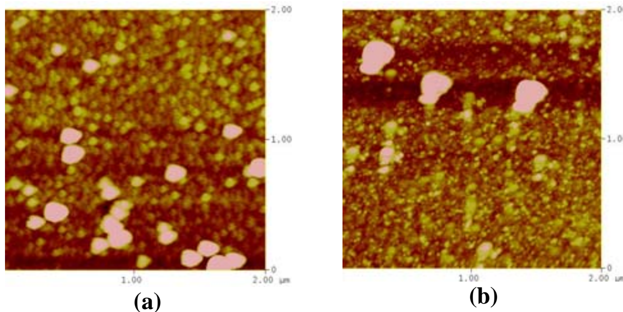
(a) (b)

Fig. 6: AFM image of Si/Ge/Zr/C (a) pristine and (b) 1×10^{14} ions/cm^2 irradiated samples.



(a) (b)

Fig. 7: AFM image of Si/Ge/Nb/C (a) pristine and (b) 1×10^{14} ions/cm^2 irradiated samples.



(a) (b)

Fig. 8: AFM image of Si/V/Ge/C (a) pristine and (b) 1×10^{14} ions/cm^2 irradiated samples.

The insignificant values of surface roughness ensure that the observed broadening in the RBS spectra is indeed due to interface mixing and not due to the roughness. From GIXRD pattern it is observed that the peaks are at the same value of 2θ for pristine as well as irradiated samples which indicated no new crystalline phase formation during mixing. The mixed part may be in the amorphous form.

According to the thermal spike model [2], the electronic subsystem is excited by the incident ions and this leads to the evolution of high transient temperature in the electronic subsystem. At a later time, the excited electrons transfer their thermal energy to the lattice via electron phonon coupling. This results in a rapid rise in the temperature upto ~10^4 K. A thermal spike is generated in the lattice subsystem for very short time duration of fraction of picoseconds (ps) to about 100 ps. Both the layers at the interface reach their transient molten state during the transient temperature spike in the lattice, which results in inter-diffusion and hence in mixing [14]. We have estimated the inter-diffusion coefficient using the following relation;

$$D = \Delta\sigma^2_{SI}/2\tau_s,$$

where τ_s is the duration of the transient melt phase

and $\Delta\sigma^2_{SI}$ is a mixing effect of single ion defined as

$$\Delta\sigma^2_{SI} = k/(\pi \times r_t^2),$$

where k is the mixing rate given by $k = \Delta\sigma^2(\phi)/\phi$, r_t is the radius of molten ion track.

We calculated inter-diffusion coefficient by taking *k* as 73.3 nm^4 for the Zr/Ge system irradiated by 120 MeV Au ions. The value of r = 7 nm and τ_s = 0.35 ps is taken for Zr from Fig. 9. The value of inter-diffusion coefficient D_{Zr} is estimated to be ~10^{-7} m^2 s^{-1}. This value is characteristics of liquid phase and hence mixing is due to transient inter-diffusion in the molten ion track thus supports the thermal spike model of mixing.

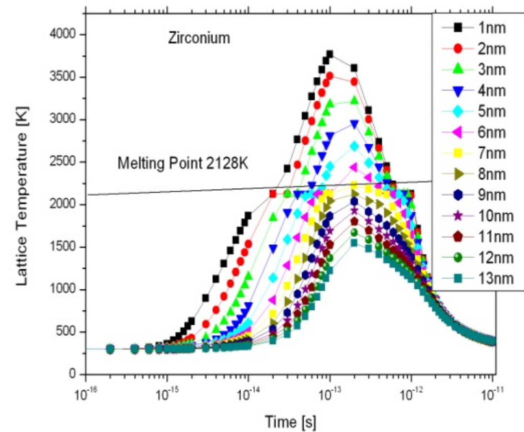


Fig. 9: The evolution of lattice temperature with time in 120 MeV Au ions irradiated Zr as calculated by thermal spike model.

4. CONCLUSIONS

The present work describes the mixing behavior of some transition metals (Zr, Nb and V) bilayers with the semiconductor germanium, deposited on the silicon substrate, due to SHI irradiation of 120 MeV Au ions. Although the mixing width increase almost linearly with increase of ion fluence, the overall mixing rate of Zr/Si, Nb/Si or V/Si shows a decreasing trend indicating the dependence of mixing on the magnitude of negative heat of mixing. GIXRD pattern does not indicate any new crystalline phase formation due to

irradiation. Therefore we can conclude that the mixed part is in amorphous form.

5. ACKNOWLEDGEMENTS

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