1. INTRODUCTION

The synthesis of buried compound layers and modification of materials for the controlled deposition of impurity atoms in a pre-selected depth region at well-defined concentrations is the most prominent application of ion beams in materials and is widely used for electrical or optical doping of semiconductors. Besides the implanted impurity atom, which modifies the material, the energy deposited into the solid along the ions trajectory may result in significant changes of the materials structure and its properties. Amorphisation and recrystallisation due to ion irradiation are well-known examples for such effects; materials modification due to surface sputtering and ion beam mixing also belong to this category. The latter effects are based on long-range atomic transport processes induced by the ion irradiation.

In the nuclear stopping regime (ion energies of the order of keV/amu), at least the ballistic transport induced by the elastic ion-target collisions is obvious. With ion energies of the order of MeV/amu, the electronic stopping regime, however, the ion loses its kinetic energy almost exclusively by electronic excitation and ionisation of the target atoms, and hence, direct atomic displacements do not occur. The irradiation with such high-energy ions, strong changes in the structure and morphology were observed for a variety of materials. Insulators, especially, were found to be very sensitive to electronic energy deposition. In these materials, the energy deposited by a single ion along its path could lead to the generation of a cylindrical amorphous track (latent nuclear track) of some nm in diameter, which often is assumed to result from transient melting and rapid resolidification of the material in the vicinity of the ion trajectory.

Study of transition metal silicides has attracted researchers for their technological applications as contact materials, gate electrodes or interconnect materials in microelectronic devices. Downsizing of devices to sub-0.18 mm scale has shown limitations to earlier popular silicides like TiSi2. Different transition metals have already been tried to form silicides, which are widely used in microelectronics and other applications, for example, vanadium silicides with different phases (V, Si, V, Si, V, Si, V, Si), where VSi shows an interesting combination of refractory properties and good electrical conductivity. Similarly, β-FeSi2 is a direct band gap semiconductor with Eg, 0.85-0.87 eV and has many applications for very large-scale integration (VLSI), ultra large-scale integration (ULSI). Another very important transition metal is cobalt whose silicides have been widely used due to their low resistivity (10-20 μΩcm), good thermal stability, and very good lattice match with silicon to grow as epitaxial layer.

Amongst the different synthesis techniques adopted to grow metal silicides, swift heavy ion beam mixing (SHIBM) with post-annealing is becoming more attractive in terms of spatial selectivity, precise control, and low-temperature process. While the ion-beam mixing (IBM) with lower energy ion has been well understood with basic accepted mechanism being the nuclear energy loss, the mechanism of SHIBM, which started in early nineties, is being studied in detail by analysing different types of systems.

The mixed phases of metal-silicides formed by SHI
finds wide applications in fabrication of microelectronic devices\(^3-6\). Apart from being technologically important the behavioural changes that take place when energetic ions lose their energy, also required to be thoroughly investigated. The authors have also reviewed their work, which they had undertaken for similar transition metals like, \(V\), \(Fe\) and \(Co\), as a series work to study the \(Si/V/\)Si, \(Si/Fe/\)Si and \(Si/Co/\)Si systems, which might give an overall trend in mixing behaviour of similar transition metals with \(Si\) due to SHI. \(Fe/\)Si is a well-known system studied by many researchers\(^12-16\) but \(V/\)Si and \(Co/\)Si is quite new where not much work has been done\(^17\). It is also intended to quantify mixing in terms of mixing rate, and thereby calculating diffusivity for each case, with the help of SIMS and RBS\(^18-19\). In case of \(Si/Co/\)Si, the SIMS depth profile gives the signature of some buried compounds formation which are further probed by XRD and Raman spectroscopy.

2. EXPERIMENTAL

For our experiment, the thin film samples were prepared by depositing the transition metal (\(Me = V\), \(Fe\) or \(Co\)) on \(Si\) wafer using electron beam evaporation technique under UHV condition at a base pressure of 1.5x10\(^{-8}\) torr. The wafers were properly cleaned and chemically etched prior to deposition. To avoid the interference of the native silicon oxide layer in ion beam mixing, a layer of amorphous \(Si\) was deposited on the substrate. Then approximately 50–60 nm thick metal (\(Me = V\), \(Fe\) or \(Co\) was deposited on this \(Si\) layer without exposing the deposited \(Si\) to atmosphere. Finally, an amorphous \(Si\) protective layer was deposited to avoid the oxidation of the metal layer. The pressure in the evaporator remained ~3x10\(^{-8}\) torr during deposition.

\(Au\) ions 120 MeV were used to irradiate the \(Si/Me/\)Si (\(Me=V\), \(Fe\), \(Co\)) samples using 15 UD Pelletron at NSC, Delhi. The fluences used were varied between 1x10\(^{15}\) and 1x10\(^{14}\) ions/cm\(^2\). The samples were mounted on a heavy copper ladder with good thermal contact using a thermally conducting adhesive, ensuring negligible increase in sample temperature during irradiation. The samples were irradiated uniformly at room temperature over an area of 1cm \(\times\) 1cm by scanning the ion beam using an electromagnet scanner. The pressure in the irradiation chamber was 10\(^{-8}\) torr. The irradiation fluence was estimated by measuring the ladder current under secondary electron-suppressed geometry and taking the scanned ion beam area.

The behaviour of interface mixing was studied using two complementary techniques, viz.; RBS and SIMS. In RBS, the depth resolution was not very impressive (~10nm) and in SIMS, the depth resolution was quite good (~2nm) thus complimenting each other. The RBS experiments were performed on both the un–irradiated and irradiated samples using 1.0 MeV \(He\) beam. A quadrupole type secondary ion mass spectrometry (SIMS) was used for studying the interface profile of \(Si/V/\)Si and \(Si/Fe/\)Si. In case of \(Si/Co/\)Si a dual beam of (\(Ar^+\) and \(Ga^+\)) TOF-SIMS was used. In both the cases, the base pressure was maintained at 10\(^{-9}\)mbar during the depth profiling. The depth profiling of the \(Si/V\) and \(Si/Fe\) samples was carried out with oxygen primary ions of energy and the +ve secondary ions were collected for analysis. In case of \(Si/Co/\)Si, \(Ar^+\) ions of energy 1.0 keV with 13nA, beam current were used for sputtering and \(Ga^+\)ions of 11.0keV with 1nA was used for analysis. The incident angle was taken to be 45° to the surface normal. The optimisation of the different experimental conditions during sputtering was done, keeping in view of having the best depth resolution. The SIMS parameters remained the same for all the samples irradiated at different fluences.

Cobalt silicide phase formation owing to the SHI irradiation at different fluences was investigated by powder XRD method. A Bruker automatic powder x–ray diffractometer (D8 Advance) was used to record diffraction patterns. X-rays from the \(Cu\) target were monochromatised using a diffracted beam-graphite monochromator. Diffraction patterns were recorded by a 0–20 scan mode in the 20 range of 25°–40° in steps of 0.02° with a 1s recording time per step. Raman spectra were recorded at room temperature using the 514.5 nm line of a 4W argon laser in backscattering geometry. A single stage Jobin Yvon–SpeX HR 640 Czerny-Tuner monochromator along with a PMT was used to detect the scattered light. A notch filter was used just before the exit slit of the Raman set-up to attenuate the Raleigh lines.

3. RESULTS AND DISCUSSIONS

The layer thicknesses of the metal layers were measured from the RBS data (shown for \(Si/Co/\)Si system only, Fig.1). These were further used to normalise the depth scale of SIMS data for the measurement of mixing layer width\(^1\). In case of \(Si/V/\)Si, the top \(Si\) layer was ~ 67.5nm and a 60 nm layer of \(V\) over the substrate \(Si\) was measured. The layer thickness for the \(Si/Fe/\)Si system as determined by RBS was ~45 nm for the \(Fe\) layer. For the \(Si/Co/\)Si system \(Co\) layer was found to be ~16 nm by RBS in the pristine
case. The SIMS depth profile for $\text{Si}/V/\text{Si}$, $\text{Si}/\text{Fe}/\text{Si}$ and $\text{Si}/\text{Co}/\text{Si}$ cases before and after the irradiation are shown in Figs. 2, 3 and 4. Mixing rates were estimated for all the three systems. Mixing rate, $k$, is defined as $k = \Delta \Omega^2/F$ where $\Delta \Omega^2$ is the spatial mixing width and $\Delta \Omega^2 = \Delta \Omega^2_\text{f} - \Delta \Omega^2_\text{i}$, $F =$ maximum fluence. The $k$ values are calculated from the slope of the $\Delta \Omega^2$ vs $F$ graph (shown in Fig.5 and Table 1).

Mixing rate in case of $V$ is $k \approx 600 \text{ nm}^2$, whereas in case of $\text{Fe}$ and $\text{Co}$, mixing rates are $k\text{Fe} \approx 225 \text{ nm}^2$, $k\text{Co} \approx 125 \text{ nm}^2$, respectively. This shows that the mixing rate of $V$, $Fe$, and $Co$ with $Si$ has a decreasing tendency under SHI irradiation. From the above data, it is clear that as one increases the atomic number (or mass) in the transition metal series, the mixing rate decreases suggesting a direct correlation between the atomic number and the mixing behaviour. Considering the properties of transition metals, it is well known that with the exception of zinc, cadmium and mercury, the transition elements are much harder and less volatile. The high enthalpy of atomisation for such elements suggest one unpaired electron per $d$ orbital is particularly favourable for strong inter-atomic interaction. Therefore, greater the number of valance electrons, stronger is the resultant bonding. In the present case the number of 3$^\text{d}$ electrons increases from 3$d^1$ in $V$ to 3$d^6$ in $Fe$ and 3$d^7$ in $Co$. The energy required for the bond breakage of the transition metal atoms increases suggesting a decrease in the mixing rate.

![Figure 2. Depth profile of Si/V/Si sample before and after irradiation.](image1)

![Figure 3. SIMS depth profile of Si/Fe/Si before and after irradiation.](image2)

![Figure 4. SIMS depth profile (a) before and (b) after irradiation for Si/Co/Si system.](image3)

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<th>Types of Energy loss</th>
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<td>Si/V/Si</td>
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Figure 5. Change in spatial interface width for Si/Me/ Si with fluence.

Since the ion fluence or the energy supplied due to SHI irradiation remained same. Higher mixing rate in case of V can also be attributed to its lower heat of formation as compared to Fe and Co. The heat of formation for V ranges from ~9.3 kcal/metal–atom to ~75 kcal/metal–atom, which is more favourable than the heat of formation for Fe (~7.5 kcal/metal–atom to ~19.4 kcal/metal–atom) or Co (~13.8 kcal/metal–atom to ~24.6 kcal/metal–atom)².

Energy loss values for 120 MeV Au ions as calculated from the simulation programme SRIM for all the three cases show that the S_v values are much higher than the S_n values (Table I). Considering the S_v values of V, Fe and Co, it is seen that the energy loss is minimum (29 keV/nm) in V compared to Fe and Co with increasing order. The values of S_v in Fe and Co are above the S_v threshold for the creation of tracks. Threshold of S_v for the creation of tracks in V is not known.

For understanding the mixing mechanism under thermal spike model, the estimation of diffusion coefficient during transient temperature spike is essential. The diffusion coefficient D is defined as $D = \frac{\Delta \Omega^2}{2t_v}$, where $t_v$ = diffusion time = ($\Phi$/$\Phi_t$) $t_t$, and $t_t$ = duration of melt phases $\Phi = $ maximum fluence and $\Phi = 1/(2\tau)^2$ is the fluence for complete overlap of the ion track. For thermal spike calculations¹,⁻², the values of $2\tau$ as 3.0 nm and $t_s$ as ~1 ps for V were used, for Fe, $2\tau$ is ~4.5 nm and $t_s$ is ~0.75 ps and for Co the values for $2\tau$ and $t_s$ are ~5 nm and ~1 ps respectively. In the authors earlier paper on Si/V/Si ¹, it was shown that $D_v \approx 10^{-8}$ m²s⁻¹, which is characteristics of the liquid phase. Similar calculations for Fe and Co in Si show almost the same order of values, i.e., $D_{Fe}$ or $D_{Co} \approx 10^{-8}$-10⁻⁴ m²s⁻¹. Srivastava et al., have recently reported close resemblance of experimental diffusivities to liquid phase diffusivities. Considering the fact that liquid phase diffusivity is almost five orders of magnitude higher than solid phase diffusivity at high temperatures, it is clear that mixing has taken place in transient melt phase, which suggests that thermal spike model is responsible for mixing.

Charactrisation of the Si/Co first interface by SIMS depth profiling indicated increase in mixing width with ion fluence and possible formation of silicides. This was further confirmed by XRD and Raman spectroscopy²³.

The XRD patterns before irradiation of the sample Fig. 6(a) do not show any specific Si or Co phase peak suggesting a priori the amorphous nature of the subsequent layers, although formation of an amorphous Co layer is most unlikely. Therefore, absence of a definite Co peak may be due to very fine grain and/or texture of the Co layer deposited on the Si over layer. Figs 6(b)–6(d) show the diffraction patterns of the sample after bombardment by ions of 120MeV with doses 1×10¹³ ions cm⁻², 5×10¹³ ions cm⁻² and 1×10¹⁴ ions cm⁻², respectively. The diffraction lines of CoSi, CoSi and CoSi are observed, which confirm the formation of mixed phase of cobalt silicides. The very low intensity of the diffraction peaks indicates that the silicide layer is very thin. The Si (211) peak shown in Figs 6(b)–6(d) may be due to the formation of polycrystalline Si in and around the Si/Co/Si: (a) before irradiation and after irradiation with 120 MeV Au ions with (b) 1×10¹³ ions cm⁻², (c) 5×10¹³ ions cm⁻² and (d) 1×10¹⁴ ions cm⁻². All the three phases of cobalt silicides are observed along with some Si polycrystalline peak from the structure.
the interface region. SHI undergo energy loss owing to the inelastic electronic scattering in the interface region inducing a transient melt phase to create such phase formations\textsuperscript{2,24}. No cobalt peak, however, could be detected in the XRD pattern in this range (2\(\theta\_40^\circ\)). The peak intensity of different cobalt silicide phases, namely, \(\text{Co}_2\text{Si}, \text{CoSi}_2\) and \(\text{CoSi}\), increases with increasing ion fluences, which indicates that the extent of silicide layer formation increases with ion fluence.

Raman spectra peaks of the buried cobalt silicide layer formation is shown in Fig. 7 in the range of 300 cm\(^{-1}\)–770 cm\(^{-1}\). De-convolution of the peaks suggested, three split peaks in two regions of 330 cm\(^{-1}\) and 730 cm\(^{-1}\). The first region showed three peaks at 322 cm\(^{-1}\), 328 cm\(^{-1}\) and 338 cm\(^{-1}\) and the second region showed peaks at 706 cm\(^{-1}\), 721 cm\(^{-1}\) and 725 cm\(^{-1}\), respectively. XRD results discussed earlier had shown the presence of all the three phases of cobalt silicide, namely, \(\text{Co}_2\text{Si}, \text{CoSi}_2\) and \(\text{CoSi}\), with \(\text{Co}_2\text{Si}\) having the maximum peak intensity. Literature reports suggest\textsuperscript{25} that the Raman peaks of the phases of \(\text{Co}_2\text{Si}\) and \(\text{CoSi}_2\) are observed at 150 cm\(^{-1}\) and 220 cm\(^{-1}\), respectively. Owing to the limitations of the present Raman spectrometer, signals below 300 cm\(^{-1}\) could not be recorded. Hence the signals of \(\text{Co}_2\text{Si}\) at 150 cm\(^{-1}\) and of \(\text{CoSi}_2\) at 220 cm\(^{-1}\) could not be detected for confirmation. However, the observed Raman peaks at 325 cm\(^{-1}\) were attributed to the one-phonon LO vibration mode\textsuperscript{26} of \(\text{Co}_2\text{Si}\), while the peak at 725 cm\(^{-1}\) is attributed to the higher order combination mode\textsuperscript{26} of \(\text{CoSi}_2\). There was no cobalt-oxide related Raman peak at 670 cm\(^{-1}\). This suggests the absence of any cobalt oxide formation during epitaxial growth and any possible contamination. The two partly merged peaks Fig. 7 may be attributed to peak splitting related to lattice stress and defects created during the SHI irradiation\textsuperscript{27}. It will be recalled that the silicide formed is a buried layer with three crystalline phases. The position of the three phases within the thin layer is random, and their crystalline forms are also different. This results in a lot of internal stress leading to the observed Raman peak splitting effect. The inelastic scattering of the high-energy (120 MeV) \(\text{Au}^+\) ions created a lot of defects within the ion tracks. Hence the third Raman peaks at 338 cm\(^{-1}\) and 706 cm\(^{-1}\) are related to disorder-induced Raman scattering\textsuperscript{27}. The LO phonon becomes localized in a small volume and is then surrounded by defects at such ion doses. Considering the phase formation sequence of cobalt silicides, it is known\textsuperscript{4,28} that according to the effective heat of formation diagram for the \(\text{Co}/\text{Si}\) system\textsuperscript{26}, \(\text{Co}_2\text{Si}\) has the largest negative heat of formation at effective concentration and hence the formation of \(\text{Co}_2\text{Si}\) is expected to be most favourable. Since \(\text{Co}\) is a fast diffusing element, it is expected that the formation of \(\text{Co}_2\text{Si}\) will be dominant compared to the other two phases, which is in accordance with the present case where it is seen that the \(\text{Co}_2\text{Si}\) peak (Fig. 6) has maximum intensity, while the peaks for \(\text{CoSi}_2\) or \(\text{CoSi}\) are much weaker compared to \(\text{Co}_2\text{Si}\). The mixing at the interface owing to the SHI irradiation in the \(\text{Fe}/\text{Si}\) system is the interdiffusion at the interface during the transient melt phase in the framework of the thermal spike model\textsuperscript{11,22}. The total energy transferred by the SHI depends on the electronic energy loss and the fluence. In the case of Bhattacharya\textsuperscript{17} et al, the maximum fluence was 1 x 10\(^{14}\) ions cm\(^{-2}\), which could not create enough mixing at the interface to be detected by RBS, and hence, postannealing was required for the cobalt silicide phase formation. In the present case, fluence of upto 1 x 10\(^{14}\) ions cm\(^{-2}\) (one order higher than the previous work\textsuperscript{37}), was used and it was observed that significant mixing does take place for detection by SIMS and XRD.

4. CONCLUSION

The present work describes the mixing behaviour of three transition metals, viz. \(\text{V}, \text{Fe}\) and \(\text{Co}\), which were, buried between two \(\text{Si}\) layers, due to SHI irradiation of 120 MeV \(\text{Au}\) ions. Although the mixing width increase almost linearly with increase of ion fluence in each case, the overall mixing rate of \(\text{V}/\text{Si}, \text{Fe}/\text{Si}\) or \(\text{Co}/\text{Si}\) shows a decreasing trend suggesting a direct correlation between their atomic numbers or the number of \(d\) electrons and the mixing behaviour. The diffusivity values suggested a transient melt phase at the interfaces following the thermal spike model. In case of \(\text{Co}/\text{Si}\), it was further probed with XRD, and Raman spectroscopy to confirm the formation of cobalt silicides as buried layer even at room temperature.

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Contributors

Dr Bibhash Ranjan Chakraborty obtained his MSc in Solid State Physics from IIT Kharagpur in 1972 and PhD from Indian Association for the Cultivation of Science, Kolkata. He then joined National Physical Laboratory, New Delhi. His areas of interest are: Semiconductor materials, Vacuum science and Surface Physics including AES, XPS, ELS, LEED and SIMS. He has more than 80 publications in national and international journals. He has received many international fellowships and visited many laboratories of different countries in different capacities. Currently, he is Deputy Head of Material Characterization Division.

Dr Devesh Kumar Avasthi is the Group Leader of Materials Science and Radiation Biology at IUAC, New Delhi. He did his PhD from Panjab University, Chandigarh in 1982. After serving in DRDL, Hyderabad for about three years, he joined IUAC (then NSC) in 1986. His main research interests are 'analysis and modification of materials', and 'synthesis and engineering of nanostructures' using ion beams. He had several international collaborations with research groups in Munich, Stuttgart, Kiel, Orsay and Padova. He is a member of the international committee for the conferences on 'Ion Beam Analysis' and 'Swift Heavy Ions in Matter'. He has several conference proceedings as editor and more than three hundred research papers to his credit.