Original Article

Formation of metal silicide by swift heavy ion induced mixing at Mn/Si interface

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ABSTRACT

Swift heavy ion (SHI) beam mixing at metal/Si system forms various silicides at the interface. In the present study SHI induced mixing has been investigated at Si/Mn/Si interfaces using 120 MeVAu^{+9} ions at three different fluences of 1×10^{13}, 5×10^{13} and 1×10^{14} ions/cm^2. Specimens were characterized by Grazing Incidence X-Ray Diffraction (GIXRD), Atomic Force Microscopy (AFM), Rutherford Backscattering Spectroscopy (RBS) and Cross-sectional Transmission Electron Microscopy (XTEM) techniques before and after the irradiation. GIXRD results revealed the presence of Mn-silicide at the interface due to the atomic mixing after irradiation. AFM of the samples was used to determine surface roughness contribution to RBS. RBS and XTEM investigations confirmed Mn_5Si_2, $MnSi$ and Mn_4Si_7 silicide phases at the interface.

1. Introduction

During the last decade, lot of research work is in progress all over the world to investigate transition metal/Si interface by SHI induced mixing due to their applications in microelectronics for devices fabrication [1–4]. Among different techniques to form metal silicides swift heavy ion (SHI) induced irradiation find their effectiveness in terms of their spatial selectivity, precise control and low temperature process. SHI beam with energies of some MeV/amu lose their energy predominantly by electronic excitation and ionization of the target atom. After a short time of about 10^{-14} s part of the excitation energy is transferred to the lattice, either by electron–phonon coupling or by coulomb explosion [5]. This high energy deposition into the lattice leads to the atomic relocation and defect creation. The direct observation of these elapsed transport processes is very limited because of small volume and the short lifetime of the excited zone. Hence the indirect methods like investigations of irradiation induced atomic mixing at the interfaces of layered systems may be very helpful. In layered systems, important information about SHI induced atomic transport processes may be extracted from such irreversible inter diffusion and phase formation.

Lot of work have been done using ion beam mixing in metals [6–12] and semiconductors [13–16] to investigate various structural, electrical, thermo-dynamical and optical properties. Along with this, a vital class of studies on metal/Si

systems have concentrated on the examination of kinetics of ion beam induced modifications and the model involved in the mixing effect in context of SHI irradiation.

Manganese silicide, which is also a transition metal silicide having interesting applications in thermoelectric, opto-electronics and spintronic devices [17]. The field of spin-troncs aims at making use of the spin degree of freedom of electrons along with charge degree of freedom, for the purpose of storage and processing of information. Among different phases of manganese silicide, MnSi$_x$ ($x = 1.72$–1.75) known as Higher Manganese Silicide (HMS) shows semi-conducting nature and are highest silicon rich intermediate phases in the manganese silicon binary system. The MnSi phase exhibit metallic behaviour, whereas some other Mn–Si compounds exhibit ferromagnetism also. Due to the wide variety of properties and applications it is important to investigate the synthesis techniques involved in the formation of Mn–Si compounds. In previous studies, manganese silicide has been successfully synthesized using different methods: solid phase reaction, co-sputtering, reactive deposition epitaxy, chemical reaction, arc melting and ion beam mixing [18–24]. In the present work irradiation induced mixing effects followed by phase formation have been investigated at Si/Mn/Si interface. GIXRD, RBS, X-TEM and AFM techniques have been used to characterize structural modifications and phase formation by ion beam mixing.

2. Experimental technique

a-Si/Mn/a-Si trilayer system was prepared onto cleaned Si (1 0 0) substrate by using electron beam evaporation technique in a UHV chamber at a base pressure of $\sim 3 \times 10^{-8}$ Torr, with deposition rates of 0.1 and 0.5 Å/s for Si and Mn. The top Si layer of 60 nm was deposited to protect the whole system from oxidation. The Si/Mn/Si system was irradiated by 120 Mev Au^{+9} ion beam by using 15 UD Pelletron accelerator facility at IUAC New. The beam current was limited to 1 pnA (particle nano ampere) during irradiation in order to avoid the sample heating. The irradiation was performed uniformly for different fluences ranging from 1×10^{13} to 1×10^{14} ions/cm^2 over an area of 1×1 cm^2 by scanning the ion beam using an electromagnet scanner. According to SRIM simulation program nuclear (S_n) and electronic (S_e) energy losses ranges from $S_n = 0.56$ keV/nm and $S_e = 32$ keV/nm for Mn, whereas $S_n = 0.21$ keV/nm and $S_e = 13$ keV/nm for Si, indicating that the electronic energy loss is dominant as compared to the nuclear energy loss. Hence the observed mixing at the interface is due to electronic energy loss only.

The SHI induced interface mixing was studied and characterized using RBS measurements for depth distribution of the elements before and after irradiation using 1 MeV α-particles in a standard scattering chamber at NCCCM Hyderabad, India. It was pumped down to 5×10^{-6} Torr by a turbomolecular pump before the start of measurements. The energetic α-particles were obtained from a 3 MV Tandetron (HVEE, EUROPA) accelerator. A Si surface barrier detector placed at a backward angle of 170° detected the scattered particles. The spectra were acquired on eight K-PC based MCA. SIMNRA, a computer code was used to simulate the RBS spectra [25].
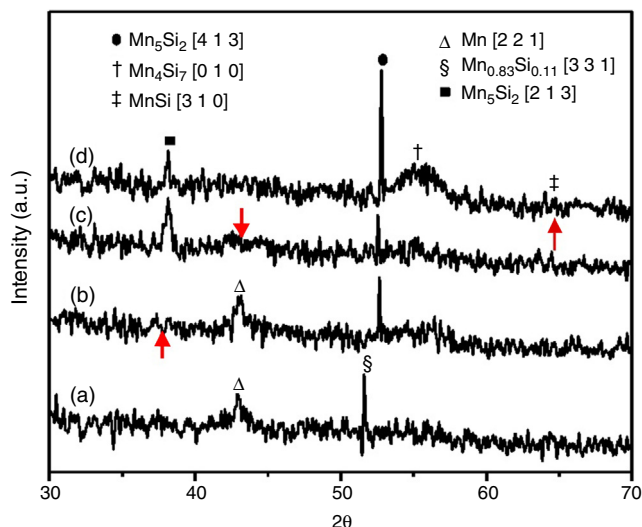

Fig. 1 – GI-XRD spectra of Si/Mn/Si films: (a) as-deposited and (b)–(d) irradiated at dose of 1×10^{13} ions/cm^2, 5×10^{13} ions/cm^2 and 1×10^{14} ions/cm^2, respectively. (For interpretation of the references to colour in this sentence, the reader is referred to the web version of the article.)

The ion beam induced transport mechanism and subsequent phase formations of unirradiated and irradiated layered thin film structure, have been investigated by Grazing Incidence X-ray Diffraction (GIXRD) at UGC-DAE-CSR, Indore.

The pristine and highest dose irradiated samples were investigated to have microstructural information, using Tecnai-G^2-20 TEM facility at UGC-DAE-CSR, Indore operating at 200 kV. The cross-sectional specimens for TEM study were prepared following the standard technique [26]. Final thinning of the sample was done using Ar ion-beam polishing. Ion beam polishing was done at 3 kV/20 μA and at a grazing incidence of 3° with respect to the sample surface.

Irradiation effect on surface morphology of the Si/Mn/Si surface was undertaken with the help of AFM in contact mode using nanoscope III E model at UGC-DAE-CSR, Indore.

3. Result and discussion

3.1. GIXRD studies

GI-XRD spectra were recorded at an incidence angle of $\sim 0.5°$ (which carries interfacial information) to identify silicide phases formed due to mixing at Si/Mn/Si interface. GI-XRD was performed using CuK$_\alpha$ ($\lambda = 1.5418$ Å) radiation in the 2θ range of 30–70° and matched with standard data using JCPDS code, as shown in Fig. 1 for un-irradiated and irradiated Si/Mn/Si samples. As-deposited sample shows two distinct peaks corresponding to virgin Mn [2 2 1] and a metastable Mn$_{0.83}$Si$_{0.11}$ [3 3 1] phase centred at $2\theta = 42.9°$ and $2\theta = 51.56°$ and the structure of Mn was found to be cubic having $a = b = c = 6.311$ Å lattice parameter. The sample irradiated at lowest fluence of 1×10^{13} ions/cm^2 shows a Mn$_5$Si$_2$ [4 1 3] silicide phase centred at $2\theta = 52.7°$ having tetragonal crystal
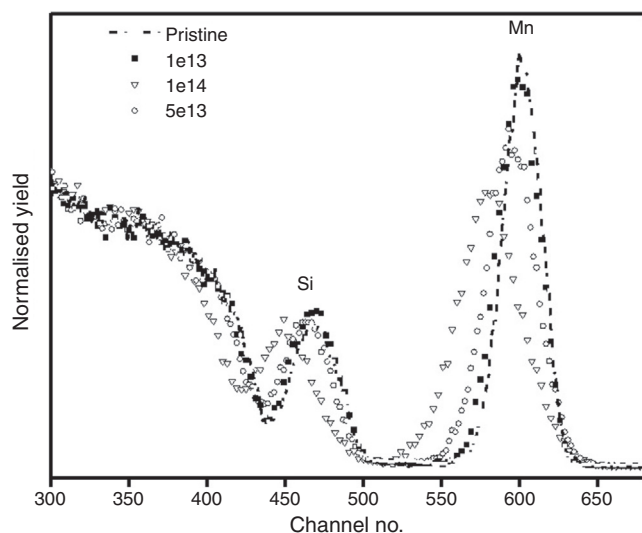
Fig. 2 – RBS spectra of as-deposited and irradiated Si/Mn/Si system.

structure with ($a = b = 8.90$ Å and $c = 8.71$ Å) along with the peak of virgin Mn (same as in case of unirradiated sample).

On comparison of these two Mn peaks there is almost no change in the intensities, suggesting Si as the most probable diffusing atomic species at this lowest fluence responsible for Mn5Si2 phase formation. At higher fluences the peak of virgin Mn has been disappeared, due to the consumption of Mn in the formation of silicides. A new peak centred at $2\theta = 38.18°$ has came into picture and can be attributed to Mn_5Si_2 [2 1 3]. It can also be observed in the figure (shown by red coloured upward arrow) that a low intensity peak corresponding to MnSi [3 1 0] starts to grow. At maximum fluence of 1×10^{14} ions/cm^2 along with the aforementioned phases an additional hump has also been observed and can be attributed to polycrystalline Mn_4Si_7 [1 0 1] phase centred at $2\theta = 55.11°$. Hence several Mn-silicides are produced by SHI irradiation at Si/Mn/Si layered sample, including metal rich Mn_5Si_2 phase, which is the probably the most stable equilibrium phase as is consistent with all the fluencies.

3.2. RBS studies

RBS spectra of Si/Mn/Si samples irradiated at 1×10^{13}–1×10^{14} ions/cm^2 fluences are compared to as-deposited, as shown in Fig. 2. Depth profiles reveal two distinct regions at higher and low energy sides corresponding to Mn and Si. It can be observed in the figure that the Mn signal height decreases with increasing fluence, which signifies diffusion of Mn into silicon. Along with diminution of the peak, tailing of Mn and Si signal towards lower energy side with increasing fluence can also be observed, representing ion irradiation induced atomic diffusion of both the species in the direction of sample interior. This is similar to the results of previously reported studies [27–29].

The simulations of the spectra have been used to determine the total thickness of the pristine sample, intermixing and subsequent phase formation at the interface due to the

effect of irradiation, using SIMNRA 6.05 program [30]. From the simulation spectrum (Fig. 3a) with raw data, the total thickness of pristine sample has been found to be ∼150 nm. Apart from this, it has also been found a small intermixed region (∼20 nm) with a metastable phase having a composition $Mn_{0.83}Si_{0.11}$. It can be assumed that at the time of deposition of the top layer the evaporated atom posses some kinetic energy which enabling it to get diffused into the metal layer. On irradiation at lowest dose of 1×10^{13} ions/cm^2 (Fig. 3b), it has been investigated that due to the migration of atoms across the interface a mixing takes place, with approximate composition of $Mn_{70}Si_{30}$ which can be attributed to probable Mn_5Si_2 phase as inferred by SIMNRA simulation code. At higher doses of 5×10^{13} and 1×10^{14} ions/cm^2, the simulated depth profiles (Fig. 3c and d) revealed that the pure Manganese has been consumed and different silicides have been formed at different depths at the interfaces. This is consistent with GIXRD results also as there was no evidence for pure Manganese. In case of highest fluence, at the interface beneath top Si layer, a first mixed layer with an approximate composition of $Mn_{70}Si_{30}$ is observed. The thickness of this layer was ∼20 nm and probably corresponds to Mn_5Si_2 silicide phase. A second mixed layer with an approximate composition of $Mn_{50}Si_{50}$ which has a thickness of ∼18 nm is produced between the first mixed layer and bottom mixed layer. A third mixed layer of approximate composition of $Mn_{36}Si_{64}$ corresponding to Mn_4Si_7 (∼15 nm) phase above deposited bottom Si layer. It was found that the mixing width was increasing with the increasing fluence.

These depth profiles are useful and instructive for an understanding of the mixing of Mn and Si atoms. They can also serve as precious tools to carry out further investigations by other techniques to interpret correctly the effects induced by the ion beam irradiation.

3.3. XTEM results

XTEM investigations on pristine (unirradiated) as well as highest dose (1×10^{14} ions/cm^2) irradiated samples were carried out for bright field imaging and selected area diffraction (SAD) modes. Fig. 4a shows the XTEM micrograph of pristine sample. The dark area in the centre of the micrograph represents unreacted Mn layer (red coloured area), a comparative less dark interfaces on both side of the Mn layer (yellow coloured area) represents silicide layer (Mn + Si) formed as a result of the reaction between Mn and Si atoms during deposition. Silicon is more electron transparent and represents the lighter area on the image.

Total thickness of the as-deposited sample was observed to be ∼150 nm from the micrograph. From SAD pattern (Fig. 4b), the occurrence of a rather diffuse innermost ring can be attributed to Mn [2 2 1], which confirms polycrystalline nature the deposited Mn. The phase identification was performed by comparing the d spacing with standard data from JCPDS files as analysed by ImageJ software which uses the formula $d = \lambda L/R$ (where L is the camera length, λ is the wavelength of electron used for imaging, R is the radius of the ring occurring in the micrograph). The micrograph (Fig. 4a) also showing the intermixed regions (Mn + Si) on either side of the central Mn layer. The interface width of the top intermixed region (∼20 nm) was approximately double then the bottom side interface (∼10 nm)
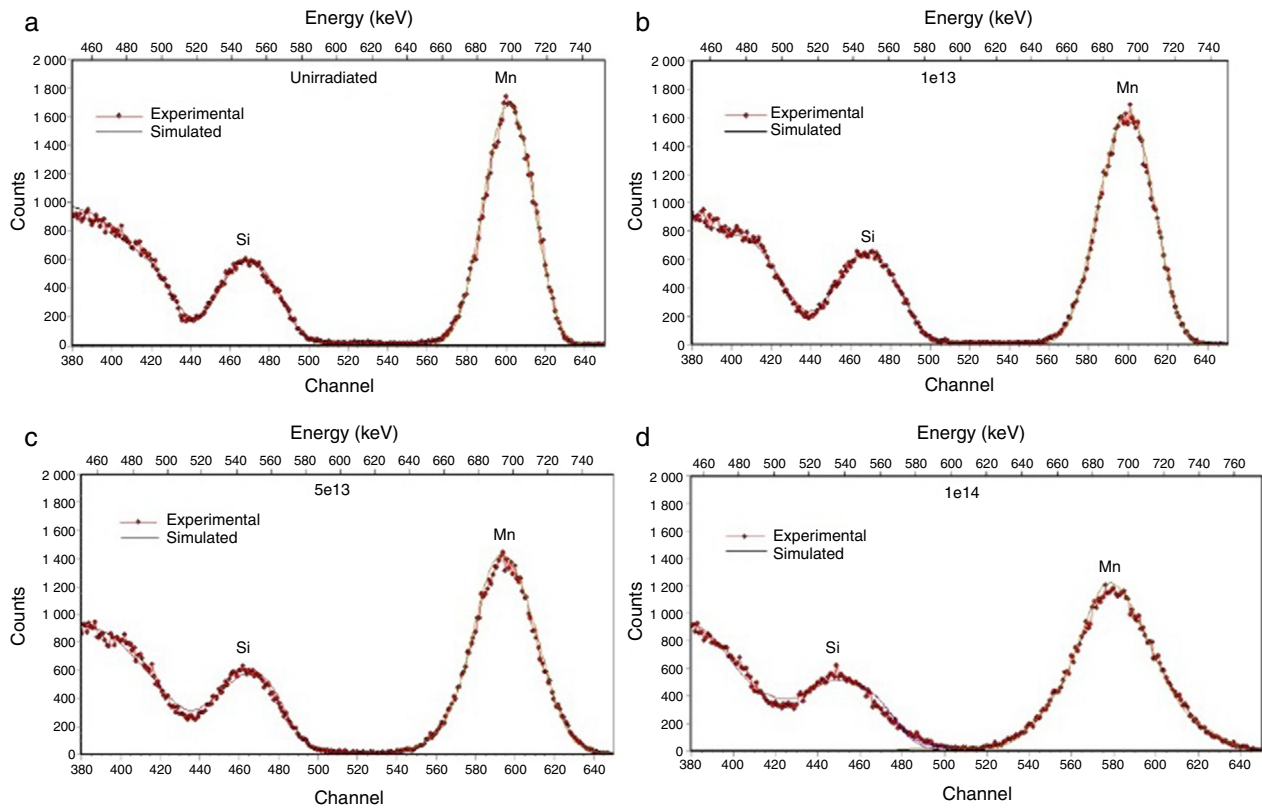
Fig. 3 – Simulated RBS spectra of (a) as-deposited sample and (b)–(d) irradiated at a dose of 1×10^{13} ions/cm^2, 5×10^{13} ions/cm^2 and 1×10^{14} ions/cm^2, respectively using SIMNRA program.
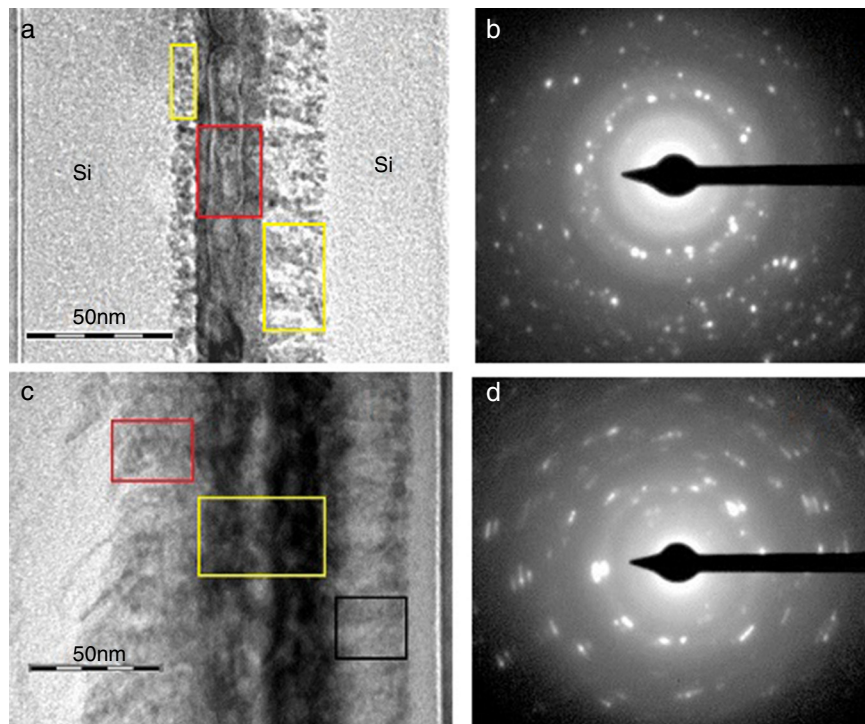

Fig. 4 – Cross-sectional TEM bright field image of (a) as-deposited and (c) highest dose irradiated Si/Mn/Si system, SAD pattern of (b) as-deposited and (d) highest dose irradiated Si/Mn/Si system. (For interpretation of the references to colour in this sentence, the reader is referred to the web version of the article.)
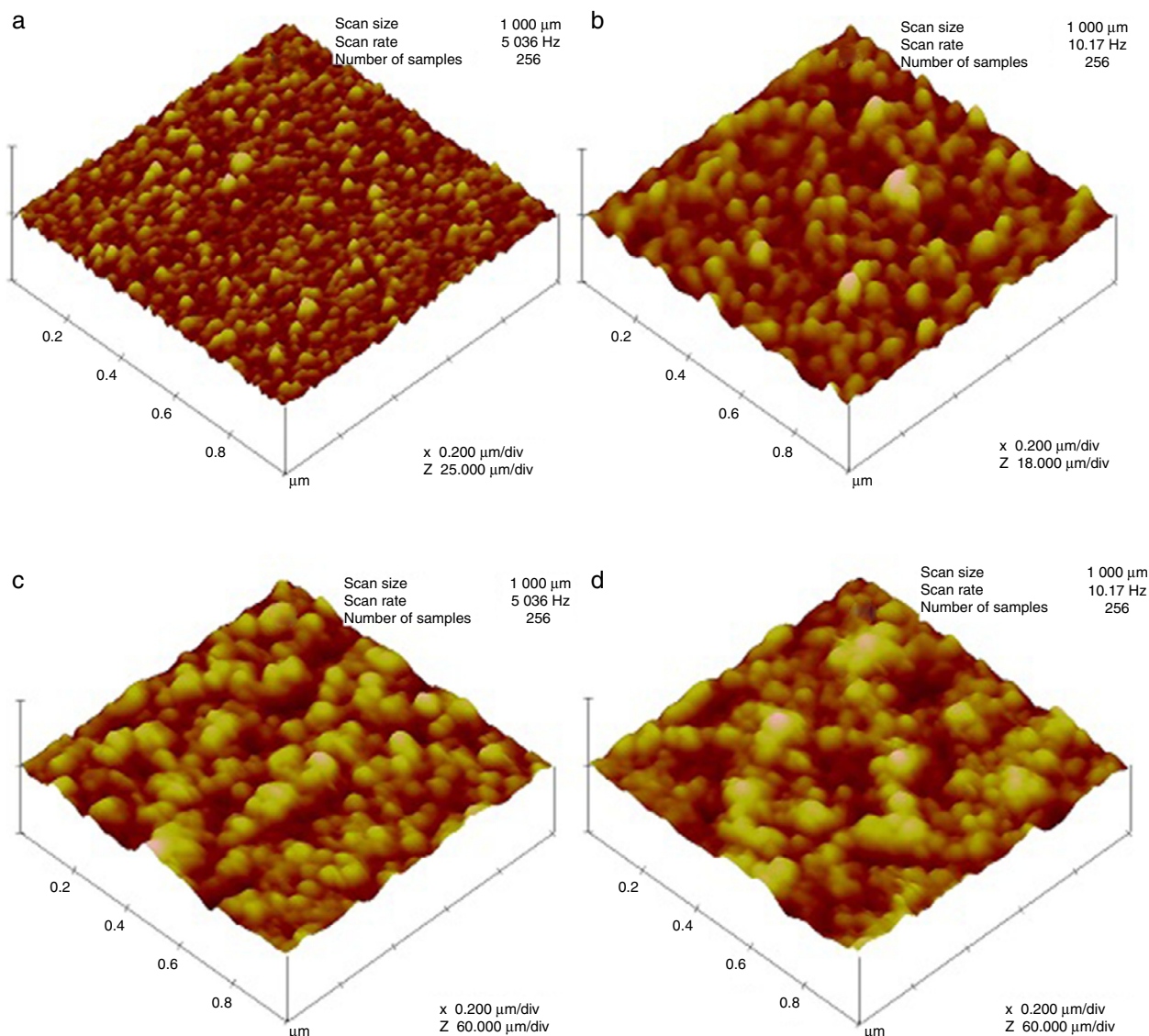
Fig. 5 – AFM micrograph of Si/Mn/Si films: (a) as-deposited and (b)–(d) irradiated at a dose of 1×10^{13} ions/cm^2, 5×10^{13} ions/cm^2 and 1×10^{14} ions/cm^2, respectively.

region. This effect can be interpreted in terms of diffusivity of the corresponding atom species. The Si is probably more mobile species as compared to the metal atoms therefore diffuses to a greater extent during deposition. The similar effects have also been reported on the same system in the context of SHI irradiation [23,31].

The irradiated sample at highest fluence of 1×10^{14} ions/cm^2 is shown in Fig. 4b and it was observed that the mixing has increased with fluence. It can be seen from the micrograph that the bottom Si layer has been participated/consumed dominantly for the silicide formation in the mixing process rather than top Si layer. The reason for this may be due to the fact that Si atoms were not free to react with metal because of the presence of oxygen in the top Si layer due to the contamination. This fact was investigated in the RBS simulation but not discussed there. The textured growths of multiple phases were observed from SAD pattern in Fig. 4d. The silicide phases formed at highest

fluence corresponds to Mn$_5$Si$_2$, MnSi and Mn$_4$Si$_7$ phases of ∼40 nm, ∼50 nm and ∼30 nm as marked by red, yellow and black coloured area, respectively, in Fig. 4c as analysed by ImageJ software. The results obtained from XTEM technique have been found to show good qualitative agreement with the results obtained earlier by the RBS measurements

To understand the role of energy loss processes in case of SHI induced bilayer mixing, it has been mentioned in the literature that the interface of metal/silicon is highly sensitive to S_e. In our case, the mixing takes place in a regime where the S_e values are 55–60 times higher than the respective S_n values in Mn and Si. This indicates that 120 MeV Au^{+9} ion induced mixing at Si/Mn/Si system is predominantly a S_e mediated process. The calculated value of S_e (∼13 keV/nm) is much higher then S_e threshold (∼9 keV/nm) for Si and therefore it is expected to get severely modified to the high deposited energy density. The S_e threshold value for Mn is not available, but since mixing rate in this case is very high (∼1000 nm^4) [32,33] it can be

predicted that the threshold in Mn must be exceeded. Thus it can be assumed that Si and Mn atoms inter-diffusion across the interface during the transient melt phase according to the thermal spike model (TSM).

3.4. AFM results

The roughness of the top layer of pristine and irradiated samples is determined by atomic force microscopy (AFM). AFM image of the system studied in the present work is shown in Fig. 5. The films exhibited smooth surface morphology with an r.m.s. roughness of about 1.065 nm in case of unirradiated specimen. The highest dose irradiated specimen exhibit r.m.s. roughness value of about 2.942 nm. The pronounced surface roughness was assigned to a rapid change of the local density, the inter-diffused silicon being consumed in the growth of Mn-silicides. From AFM results, we observe that there is insignificant difference between the roughness of pristine and irradiated samples. Therefore it is safe to assume that the observed changes at the lower energy edge of Mn and Si (in RBS spectra) are not due to the surface roughness and are solely due to the mixing at the interface.

4. Conclusion

In the present work mixing behaviour of 120 MeV Au^{+9} ion irradiated Si/Mn/Si thin film system has been investigated at varying fluences of 1×10^{13}, 5×10^{13} and 1×10^{14} ions/cm^2. GI-XRD and RBS analysis shows that the mixing takes place at the interface and increases with the irradiation dose. XTEM micrograph directly shows different layers corresponding to different phases of Mn–Si system, confirming the mixing of Si/Mn/Si thin film. These results revealed that the mixing takes place at both the interfaces, due to the dominance of electronic energy deposition. Multiple silicide phases have been formed at the interface due to the atomic migration of the atom enforced by SHI irradiation. Among them Mn$_5$Si$_2$ was the most stable and dominant phase.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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