Irradiation Induced Modifications in Magnetic Property of Mn/n-Si Structure

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Abstract:
Mn films of ~50 nm were deposited on n-Si (100) substrates by electron beam evaporation technique. The Mn/n-Si structures were irradiated from swift heavy ions with a fluence of $1 \times 10^{13}$ ions/cm$^2$. The irradiated and unirradiated structures have been characterized from atomic force microscopy, X-ray diffractometry and vibrating sample magnetometer facilities. It has been found that surfacial/interfacial granular magnetic silicide phases (of Mn$_x$Si$_y$) are formed before and after the irradiation with irradiation induced modifications of surface morphology and magnetic property. The surface roughness has been found to decrease on the irradiation from the atomic force microscopy data. From the X-ray diffraction data, it has been found that after the irradiation MnSi is formed in addition to Mn$_5$Si$_2$ as compared to unirradiated ones. The magnetization characteristics show that the magnetic parameters such as coercivity, saturation magnetization, remanance and squareness have decreased on the irradiation for in-plane orientation whereas coercivity and remanance is increased after the irradiation for out of plane orientation. The increase of remanance shows the presence of strong exchange coupling in the structure after the irradiation.

1. Introduction:
Recently, magnetic thin films on semiconductor substrates have attracted considerable attention due to its significant role in spintronics. Utilizing the spin of the electron in semiconductor devices holds great potential to provide high-speed device structures [1]. Spin injection from a magnetic metal to a semiconductor is one of the significant key processes for spintronics [2]. For such applications, magnetic metal/Si heterojunctions have attracted much attention and would be highly desirable to grow epitaxial ferromagnetic films on Si substrates. There have been some reports on this issue, concerning the epitaxial growth of Fe on GaAs, and the injection of spin-polarized electrons from a metal into a semiconductor [3, 4]. However, such systems are also susceptible to intermixing which causes the formation of nano cluster magnetic phases whose magnetic properties are of fundamental and technological significance.

Manganese is a magnetic element and reacts easily with Si to form manganese silicide. Among the manganese silicides, attention has been focused on the MnSi, Mn$_5$Si$_2$ and Mn$_5$Si$_3$. MnSi [5] is ferromagnetic with a curie temperature of 30K, Mn$_5$Si$_2$ [6] is antiferromagnetic, Mn$_5$Si$_3$ [6] is known to be paramagnetic and MnSi$_{1.71}$ is a higher manganese silicide (HMS) of MnSi$_{2-x}$ (x: 0.25 ~ 0.27) which is a narrow band gap semiconductor. Magnetic properties of these grown or deposited silicides are strongly dependent on microstructure and hence the magnetic properties can be tailored by modifying the microstructure. Swift heavy ion irradiation is an excellent tool for tailoring [7] the microstructure as a result of irradiation induced thermal spike phenomenon [8]. Thermal spike phenomenon of the irradiation...
results in the recrystallization and growth phenomena in the irradiated structures to modify the microstructures [9]. Ion beam irradiation is also known to modify the extrinsic magnetic properties, such as magnetic anisotropy, coercivity and magnetic exchange coupling [10-14].

In order to achieve the growth of these silicides on silicon substrate and to investigate the magnetic properties of these magnetic silicides interfacing with silicon, the Mn/n-Si interfaces have been prepared and irradiated from swift heavy ions with a fluence of ~1x10^{13} ions/cm^2. The structures have been characterized from atomic force microscopy (AFM), X-ray diffractometry (XRD) and vibrating sample magnetometer (VSM) to investigate the magnetic property in relation to the microstructures.

2. Experimental details:
n-Si (100) wafers of 8-10 Ω-cm resistivity have been used for the fabrication of Mn/n-Si structure. n-Si substrates have been degreased by ultrasonic cleaning in trichloroethylene (TCE) solution and then etched by diluted HF for 15 sec. and then dried in a clean air chamber for the metallization. A thin layer (of ~ 50 nm) of Mn (99.99 % purity) was deposited on the n-Si substrates in a 1 cm x 1 cm area. The above fabricated Mn/n-Si interface structures were irradiated at room temperature from the Mn layer side (fronting the beam) by 100 MeV Fe^{7+} ions with a fluence of ~1x10^{13} ions/cm^2, at Inter University Accelerator Centre, New Delhi from 15 UD pelletron facility. The ion beam was made incident 30° off-normal upon the samples during the irradiation for the wider exposure of the sample surface. The size of the beam spot was around 2.5 mm x 2.5 mm which was constantly scanned on the sample surface during the irradiation. The typical beam current was varied between 2 to 3 pnA (particle nano ampere).

3. Results and discussion:
Figure 1 shows the AFM micrograph (with x-y, 0.2 μm/div. and z, 100 nm/div.) of unirradiated Mn/n-Si structure of the top side of manganese film on silicon substrate. The observed feature in the micrograph shows the grainy microstructure where the grains are observed to be overlapping with each other. Figure 2 shows the AFM feature (with x-y, 0.2 μm/div. and z, 100 nm/div.) for the irradiated structure which also shows nice ellipsoidal shaped granular particles. The grains are well resolved without overlapping which could be formed due to the irradiation induced melting and recrystallization phenomena [9]. Moreover, the grains seems to be embedded in silicon substrate.

![AFM micrograph of unirradiated structure.](image1)

![AFM micrograph of irradiated structure.](image2)

AFM image clearly shows the decrease in roughness after the irradiation. It is found to decrease from 15.3 nm to 7.8 nm after the irradiation as compared to unirradiated ones. Moreover, roughness is a measure of the texture of a surface. It is quantified by the vertical deviations of a
real surface from its ideal form. If these deviations are large, the surface is rough; if they are small the surface is smooth. The AFM features of the irradiated ones (figure 2) clearly shows that grains are well shaped, resolved and there is no protrusion in horizontal or vertical direction on the scale of 1µm x 1µm. It clearly appears from figures 1 and 2, that the surface roughness is reduced after the irradiation (in figure 2 as compared to figure1). The smoothening mechanism on the surface during ion irradiation include volume diffusion, viscous flow, sputter redeposition and sputter removal affected by shadowing processes [15].

In order to identify the formed silicide phases, XRD data have also been recorded. For XRD, Cu alpha 1 (\(\lambda = 1.54439\) Å) is used as an x-ray target. XRD pattern for the unirradiated and irradiated structures are shown in figure 3 and figure 4, respectively. The data of figure 3 shows two distinct peaks of Mn\(_5\)Si\(_2\) whereas the data of figure 4 show that there are five distinct peaks of Mn\(_5\)Si\(_2\)/MnSi. It is further observed that the intensity of Mn\(_5\)Si\(_2\) (213) has increased and the intensity of Mn\(_5\)Si\(_2\) (331) has decreased after the irradiation as compared to unirradiated ones. Moreover, it is also interesting and significant to observe the evolution of two new peaks of MnSi after the irradiation, i.e., MnSi (310) and MnSi (321). The evolution of new phases of manganese silicides can be understood due to the irradiation induced interfacial intermixing. The crystallite size estimated from Scherrer relation [16] shows a decrease of crystallite size after the irradiation. For one of the peak it is found to decrease from 310 nm to 161 nm after the irradiation. The observed features from AFM and XRD could be understood in the realm of irradiation induced strong interfacial intermixing to cause the microstructural modifications. Swift heavy ion induced interfacial modifications has been earlier shown by Bolse [17].

The magnetization characteristics of the structure (i.e., Mn film deposited onto n-Si substrate) have been measured from vibrating sample magnetometer (VSM). The VSM measurements have been done at room temperature. Figures 5a, b, 6a and b show the M-H behavior for the unirradiated and irradiated ones for the applied magnetic field parallel and perpendicular to the plane of the structure, i.e., along and across the interface. The parameters of magnetization behavior are listed in table 1.

It is interesting to observe that in-plane seems to be the easy axis of magnetization whereas out of plane seems to be the hard axis of magnetization. It is also interesting to observe room temperature ferromagnetism in the unirradiated/irradiated structures of Mn/Si. The origin of ferromagnetism in the manganese silicide is known to be due to the small amount of carbon atoms incorporated into the paramagnetic Mn\(_5\)Si\(_2\) [18]. In the case of silicon crystals, there is always presence of some carbon impurities which may play role to cause the observed room temperature ferromagnetism. The dissolved carbon in our silicon substrate has been found by our several EDAX and IR studies in various contexts [19]. The origin of ferromagnetism has been understood by Takeuchi et al. [20] as the effect of the anisotropic modifications of the local structure around the manganese sites by the carbon (C) atom. It is
possible that the irradiation may change such modifications to change the magnetic property as observed for the irradiated structure.

**Table 1 Magnetic parameters of Mn/n-Si structure**

| Magnetic parameters | In-plane orientation of Mn/Si | Out of plane orientation of Mn/Si |
|---------------------|-------------------------------|---------------------------------|
|                     | Unirradiated                  | Irradiated (1x10^{13} ions/cm²) | Unirradiated | Irradiated (1x10^{13} ions/cm²) |
| Hc (Oe)             | 80.67                         | 69.45                           | 189.69       | 237.13                           |
| Ms (emu)            | 6.6 x 10^{-4}                 | 2.5 x 10^{-4}                   | 5.2 x 10^{-4} | 3.1 x 10^{-4}                   |
| Mr (emu)            | 7.9 x 10^{-5}                 | 1.9 x 10^{-5}                   | -4.7 x 10^{-6} | 6.9 x 10^{-6}                   |
| S = Mr/Ms           | 0.119                         | 0.077                           | 0.077        | 0.023                           |

However, the saturation magnetization is reduced after the irradiation for both the orientations of the applied magnetic field. This can be understood by evolvement of the MnSi silicide phase, which is known to be paramagnetic at room temperature. There is a possibility that due to the enhancement of paramagnetic phase there is a reduction in the saturation magnetization after the irradiation. Moreover, for in-plane orientation, other magnetic parameters such as coercivity, remanence and squareness are found to decrease after the irradiation, whereas, for out of plane magnetization, coercivity and remanence is found to increase on the irradiation. The increase in coercivity and remanence for the out of plane magnetization can be understood by considering the out of plane oriented grains of the magnetic silicide phases. The AFM features of the irradiated structures (figure 2) reveals such possibility. Moreover, the AFM features clearly show the shape anisotropy which shall result the observed differences for in plane and out of plane magnetizations.

**Figure 5** M-H characteristics of unirradiated structure for in-plane magnetic field (a), and for out of plane magnetic field (b).

**Figure 6** M-H characteristics of irradiated structure for in-plane magnetic field (a), and for out of plane magnetic field (b).

4. Conclusion:
It is found that ion beam irradiation modifies the surface morphology and magnetic property of Mn on Si substrate. Surficial/interfacial granular/ellipsoidal shaped silicide phases have been observed to grow on the irradiation with paramagnetic Mn₅Si₂ and ferromagnetic MnSi silicide phases. Surface roughness has
been found to decrease on the irradiation. The microstructural changes on the irradiation have been understood in the realm of swift heavy ion induced interfacial intermixing processes. The irradiation induced changes of coercivity and remanence seems to be due to the oriented grains of MnSi silicide phase which are formed on the irradiation.

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