Implanted manganese redistribution in Si after He^+ irradiation and hydrogen pulse plasma treatment

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Abstract. Si-Mn alloy with a Mn content of a few percent is potentially a candidate for room temperature (RT) dilute magnetic semiconductor (DMS). However, the present methods of material manufacture suffer from problems with poor Mn solubility and thermodynamical limitations. We study a non-equilibrium method in which silicon is first implanted with 160 keV manganese ions to a dose of 1×10^{16} ions/cm^2 and next either irradiated with 1.5 MeV $^4He^+$ ions from the Warsaw Van de Graaff accelerator at 400°C or treated with high-energy hydrogen plasma pulses. Conclusion from Rutherford backscattering spectrometry (RBS) examination of the samples is that both approaches lead to recovery of crystalline surface layer with manganese occupying off-substitutional sites. The potential development of the method is discussed.

Key words: dilute magnetic semiconductors (DMS) • Mn-implanted Si • ion beam induced epitaxial crystallization (IBIEC)

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Introduction

Devices exploiting electron spin (spintronics) require materials in which free electron spin can be suitably controlled by external electric and/or magnetic fields [23]. DMS are considered as potential candidates for such applications. These materials combine semiconducting properties with possibility to form ferromagnetic layers. Suitable candidates are selected from standard elemental semiconductors/semiconducting compounds with a significant admixture of a transition metal (TM) like Mn or Cr providing localized spin. A number of such materials have been found and described in the literature, a typical example being $Ga_{1-x}Mn_xAs$ with x of the order of a few percent [8].

DMS should operate at or above RT in actual spintronics applications. However, most of the DMS's developed thus far exhibit transition to ferromagnetic state at some temperature T_c far below DMS's with high T_c.

The technology of DMS's manufacture faces a common problem: incompatibility of the required relatively high TM content with solubility limits at thermal equilibrium. Because of such limits the TM content may precipitate in the course of the growth process forming a second phase (e.g. MnAs in $Ga_{1-x}Mn_xAs$ [16]). To avoid the equilibrium problems, the growth process may be carried out in thermal conditions far from equilibrium. Thus, ferromagnetic $Ga_{1-x}Mn_xAs$ may be grown by molecular-beam epitaxy (MBE) at low temperatures (LTMBE [22]).

Another method to avoid the equilibrium problems is to introduce the TM content using some inherently non-equilibrium process like ion implantation. However, at the doses required for ferromagnetic interaction to occur, ion implantation introduces a significant lattice damage that may impact semiconducting and ferromagnetic properties of the processed material. Such damage is usually cured by thermal annealing commonly applied after ion implantation. Unfortunately, typical thermal annealing itself is an equilibrium process that may lead to precipitation of unwanted phases.

The precipitation problems can be relaxed if thermal annealing is carried out sufficiently fast thus inhibiting the progress of new phase formation. Single pulse rapid thermal annealing (RTA) technique has been applied for this purpose and annealing times as short as 30 s can be achieved [2].

Very high rates of annealing can be attained if pulse laser melting (PLM) is used [18]. In the technique crystal surface is rapidly molten by an excimer laser pulse and crystallizes within a few hundred nanoseconds. Indeed $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xP$ with ferromagnetic properties have been recently synthesized by that method [15].

Pulsed plasma beams may be a convenient alternative to PLM annealing. The technique offers a greater treatment area and a possibility of co-depositing other materials [13, 14].

Still another approach to annealing of ion-implanted crystals is referred to as ion beam induced epitaxial crystallization (IBIEC) [19]. In this technique crystal amorphized to some depth by ion implantation is irradiated at elevated temperatures with a beam of some energetic ions. Mobile defects created by the latter beam interact with the crystalline bulk-amorphous surface layer boundary and the boundary retracts to the surface leaving the layer re-crystallized. The IBIEC process is thermally activated and proceeds with an activation energy much lower than the activation energy for thermal annealing [20]. It is not clear whether the IBIEC process should be considered as a thermal-equilibrium-one and whether it leads to precipitation of extra phases. In some cases metal silicides were reported to grow in IBIEC-processed implanted Si [6]. However, in a recent paper [4] Chen reported that ferromagnetic $Ga_{1-x}Mn_xAs$ formed in Mn-implanted GaAs irradiated with 350 keV He^+ ions at 250°C exhibited the transition temperature of 270 K, far above the results in LTMBE material.

This paper reports our studies performed on silicon as a material with best recognized technological properties and merits. As a matter of fact, the existing theory based on the Zener model and carrier-mediated ferromagnetism [7] predicts Si transition temperature as low as 140–150 K. However, experimental data are more optimistic. Bolduc [3] and Yoon [21] reported $T_c > 400$ K in Mn-implanted Si RTA-annealed at 800°C and 650°C, respectively, for 5 min. In both cases no hard evidence was presented that the observed ferromagnetism did not originate from precipitates found in Mn-implanted Si by other authors [1]. Results obtained on PLM-treated Mn-implanted Si [11] suggest substitution of Si by Mn.

Since results obtained on IBIEC-annealed Si implanted with various dopants [9, 10, 17] are encouraging, we decided to examine the potential of that annealing method with respect to Mn-implanted Si. We also examined pulsed plasma treatment from the viewpoint of DMS preparation.

Experimental

Czochralski p-type silicon wafers of (111) orientation and resistivity of 150 Ωcm were cut into 10 × 10 mm samples and implanted at RT with 160 keV Mn^+ ions to a total dose of 10^{16} ions/cm^2. Next, the samples were irradiated at 400°C with 1.5 MeV $^4He^+$ ions from the Warsaw van de Graaff accelerator to doses ranging from 1.5×10^{16} to 7×10^{17} $^4He^+$ ions/cm^2. Another set of samples was irradiated with two about 1 μs long hydrogen plasma pulses of energy density 2.5–4 J/cm^2. The pulses were generated by the IBIS device [13]. The samples were then analyzed by the RBS technique at the Rossendorf Ion Beam Centre using 1.7 MeV $^4He^+$ ion beam. Random and channeled measurements were performed. Some of the obtained experimental RBS spectra were fitted using the SIMNRA code for RBS simulations in order to simulate the Mn depth profiles.

Results and discussion

Random and channeled RBS spectra of some virgin Mn-implanted-silicon/$^4He^+$-irradiated/hydrogen-plasma-treated samples are presented in Fig. 1. The plot shows that Mn implantation produces about 90 nm thick amorphous zone. Irradiation to the lowest dose of 1.5×10^{16} He^+ ions/cm^2 leads to a complete recovery of the crystallographic order within the zone. However, the resulting surface layer, although aligned with the substrate structure, is far from being perfect, as deduced from the high value of the channeled RBS spectrum below the surface peak.

RBS spectrum for the plasma-pulse-treated sample is very similar to the virgin crystal spectrum. That means that plasma pulses almost completely recovered the implantation-damaged region.

Manganese evolution can be deduced from manganese parts of RBS spectra taken for implanted/$^4He^+$-irradiated/pulse-treated samples shown in Figs. 2a and 2b.

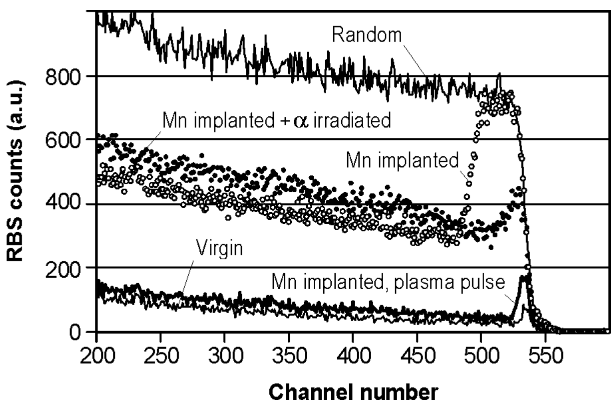

Fig. 1. Random and channeled RBS spectra corresponding to a virgin silicon sample and channeled spectra of Mn-implanted/implanted and $^4He^+$-irradiated/hydrogen-plasma-pulse-treated samples.

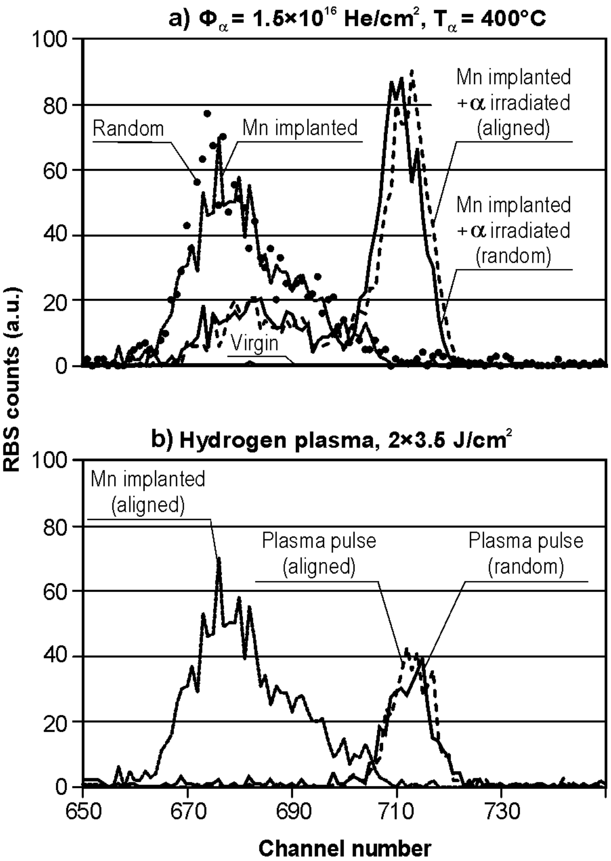

Fig. 2. Random and channeled RBS spectra illustrating manganese evolution after (a) $^4He^+$-irradiation and (b) hydrogen-pulse-plasma treatment.

In Fig. 2a we can see that a significant shift of the manganese content towards the surface occurred after $^4He^+$ irradiation. Higher dose irradiations (not shown) led to reduction of the Mn peak, i.e. produced an apparent escape of Mn from the sample. Thus, $^4He^+$ irradiation must be administered very carefully to avoid reduction of the manganese content.

Figure 2b shows the Mn content evolution after plasma pulse treatment. As before, we can see transport of manganese towards the surface. However, Mn concentration has also been reduced in comparison to the $^4He^+$ irradiation case. Plasma pulse energy applied was higher than the surface melting threshold estimated as 2.2–2.5 J/cm^2 (depending on the pulse length) and it is likely that some appropriate reduction of the energy will lead to a more favorable Mn content evolution.

Aligned spectra of $^4He^+$-irradiated and pulse-treated samples coincide with the random ones. This shows that Mn crystallizes in interstitial positions, in agreement with theoretical considerations [5]. At the present stage of our research we cannot exclude the possibility that Mn forms other crystallographic structures. What is only known is that Mn does not occupy substitutional positions in otherwise perfect crystal.

SIMNRA simulations of the $^4He^+$-irradiated Mn profiles are shown in Fig. 3. A significant Mn shift towards the surface may be seen. However, no out-diffusion is seen, as deduced from simulation of the cumulated Mn content within the sample. Although the surface layer created by irradiation is very thin, the Mn content in this layer is quite high and amounts to

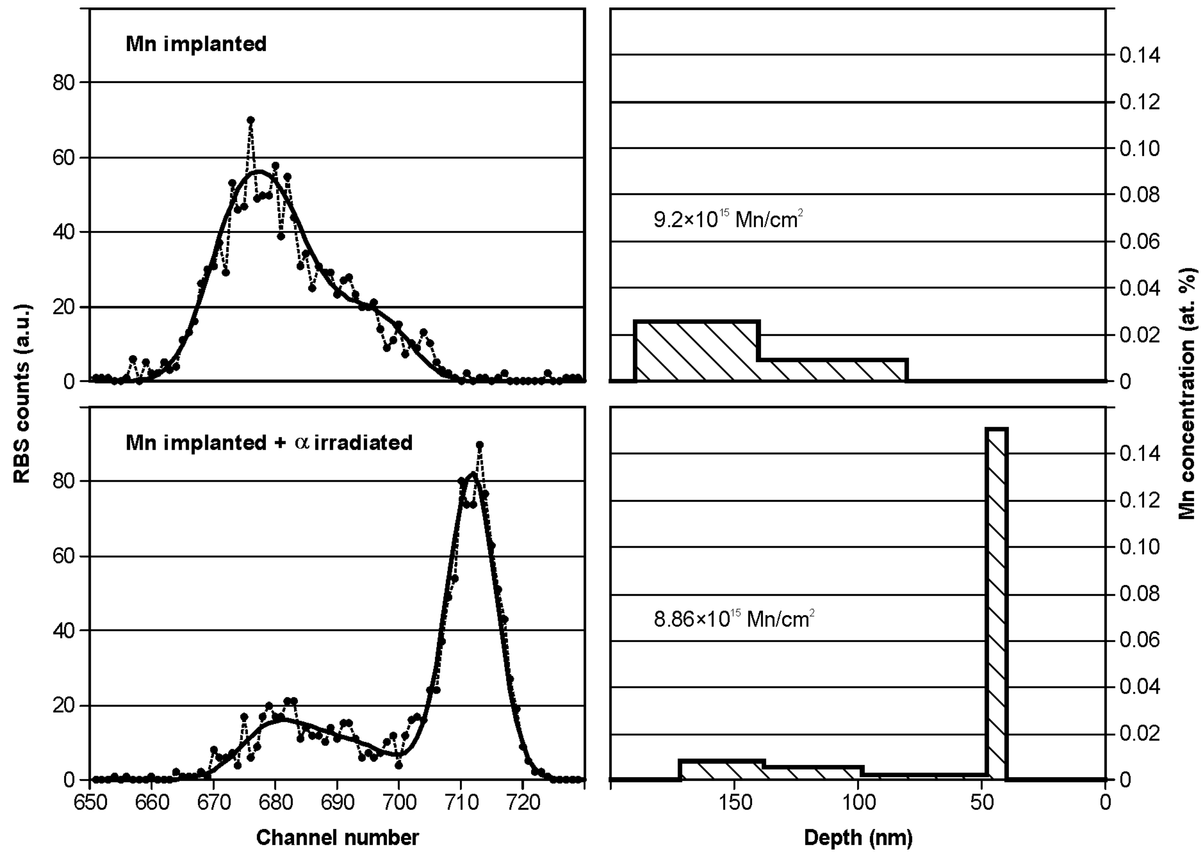

Fig. 3. Results of SIMNRA simulations of Mn profiles before and after $^4He^+$-irradiation. Left: RBS spectra. Right: Mn depth profiles (please note the depth scale direction).

14 at.%. In plasma-pulse-treated samples the surface concentration may be estimated as 7%.

The effects of $^4He^+$-irradiation at elevated temperatures may be considered as a manifestation of IBIEC. The attained crystal recovery is remarkable and allows us to conclude that with more careful adjustment of alpha particle energy/dose and irradiation temperature much better results are conceivable. However, it is also obvious that the location of manganese is not substitutional and the IBIEC process satisfied the same thermodynamical constraints which favor interstitial locations [5].

The effects of plasma pulse treatment are similar to that of $^4He^+$-irradiation but the surface layer quality seems to be better. We see no diffusion of manganese within the silicon molten phase. Again, this process should be studied in more detail because potentially the plasma treatment gives a better chance to avoid problems of second phase precipitation.

Work on determination of the manganese structure and the magnetic properties is in progress.

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