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Stress-mediated redistribution of Mn in annealed Si:Mn

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ABSTRACT

Buried amorphous silicon (a-Si) is produced in Czochralski single crystalline silicon implanted at 340 K with Mn^+ (Si:Mn, $^{55}Mn^+$ doses, $D = 2 \times 10^{15}$ or 1.2×10^{16} cm^{-2}, energy 160 keV). Stress-mediated redistribution of Mn and solid phase epitaxial re-growth (SPER) of a-Si at up to 1273 K (HT), also under hydrostatic Ar pressure up to 1.1 GPa (HP), have been investigated by SIMS, X-ray and related methods. As-implanted Si:Mn indicates magnetic ordering. SPER depends on Mn^+ dosage, HT, HP an on processing time. Processing at 870–1000 K results in a minimum in the Mn concentration at ~0.15 μm depth. At 1170 K and above, the diffusion of Mn to the surface increases with HP. Our results help in understanding the mechanisms of SPER and of origin of magnetic ordering in Mn:Si.

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1. Introduction

Ion-beam-induced formation of amorphous silicon (a-Si) and its solid phase epitaxial re-growth (SPER) during annealing of implanted crystalline silicon (c-Si) have attracted interest because of their importance for fabrication of Si devices [1]. SPER of a-Si depends, among others parameters, on temperature (HT) and hydrostatic pressure (HP) [2].

Silicon implanted with Mn^+ at about 620 K and annealed at up to 1170 K has been reported to order magnetically up to 400 K [3,4]. This is important for producing diluted magnetic semiconductors (DMS), of perspective application for spintronics.

Silicon implanted with metallic ions and processed at HT and under HP ≤ 1.1 GPa, indicates interesting properties. Processed Si:V, Si:Cr and Si:Mn show magnetic ordering, confirming DMS features [5–7]. Implantation with Mn^+ at ≤340 K results in partial amorphisation of Si near R_p (projected range of Mn^+). Subjecting Si:Mn to subsequent processing at HT–HP produces magnetically ordered materials [6,7]. In what follows we report new results on the effect of HP applied at annealing on the HT-induced structural changes in Si:Mn, mostly related to SPER of a-Si.

2. Experimental

$^{55}Mn^+$ ions were implanted at 340 K, with doses, $D = 2 \times 10^{15}$ cm^{-2} (ASi:Mn samples) or 1.2×10^{16} cm^{-2} (BSi:Mn) and energy, $E = 160$ keV, into (0 0 1) oriented p-type Czochralski silicon.

The samples were processed, typically for 1 h, in Ar atmosphere at up to 1273 K under HP up to 1.1 GPa. The depth distribution of Mn was determined by Secondary Ions Mass Spectrometry (SIMS, Cameca 6F instrument). X-Ray Reciprocal Space Maps (XRRSMs) were taken using MRD-PHILIPS diffractometer. Magnetic measurements (using SQUID magnetometer) were performed on the as-implanted samples.

3. Results and discussion

Heavy implantation of Si with energetic ions results in a creation of buried a-Si [1]. In the considered Si:Mn samples implantation resulted (TEM results, not presented here) in especially strong structural disturbances at up to 0.25 (±0.05) μm depth, related to the projected range of Mn^+ ($R_p = 0.14$ μm for $E = 160$ keV). As follows from XRRSM measurements (not shown here), as-implanted ASi:Mn exhibits the semi-layered structure composed of less damaged (about 0.05 μm thick) top layer, intermediate strongly damaged region, and the Si substrate practically not disturbed at a depth of about 0.5 μm. Dislocation loops in the {1 1 1} planes with the Burger vector perpendicular to dislocation loops were detected within c-Si in as-implanted Si:Mn.

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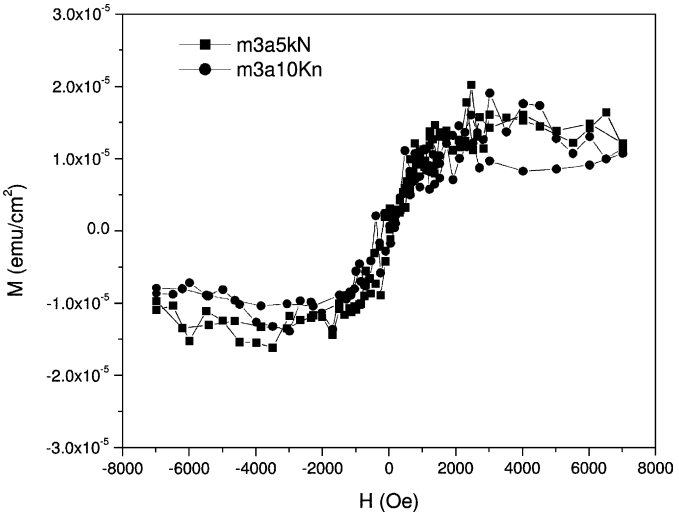

Fig. 1. Magnetisation (M) versus magnetic field (H) measured for BSi:Mn at $T = 5$ K (■) and 10 K (●). H was applied parallel to sample surface.

The formation of Mn clusters with short range magnetic order has been suggested for as-implanted Si:Mn [8]. Photoluminescence investigation of Si:Mn ($D = 1 \times 10^{16}$ cm^{-2}) confirmed almost complete amorphisation of the near-surface regions [6].

ASi:Mn prepared by low dose implantation ($D = 2 \times 10^{15}$ cm^{-2}) presents paramagnetic behaviour. In as-implanted BSi:Mn ($D = 1.2 \times 10^{16}$ cm^{-2}) magnetic ordering is observed (Fig. 1). Weak dependence of magnetization on temperature suggests magnetic ordering also at above 10 K.

Implanted Mn atoms are mainly located within the a-Si area. The depth distribution of Mn in as-implanted ASi:Mn indicates a broad maximum (Fig. 2), corresponding to R_p. Implantation with $D = 1.2 \times 10^{16}$ cm^{-2} leads to almost the same distribution of Mn with a higher peak concentration (Fig. 3).

Distinctly deeper tail of the Mn distribution, especially for the BSi:Mn sample (Fig. 3), may be caused by ion channelling during implantation.

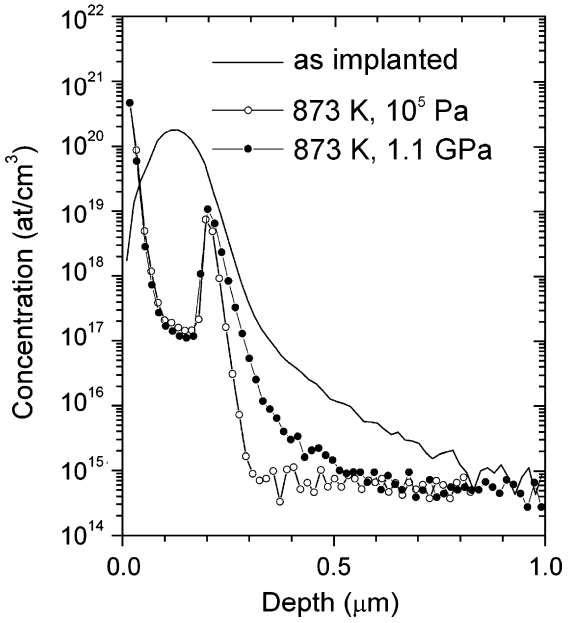

Fig. 2. SIMS depth profiles of ^{55}Mn in ASi:Mn, as-implanted and processed for 1 h at 873 K under 10^5 and 1.1 GPa.

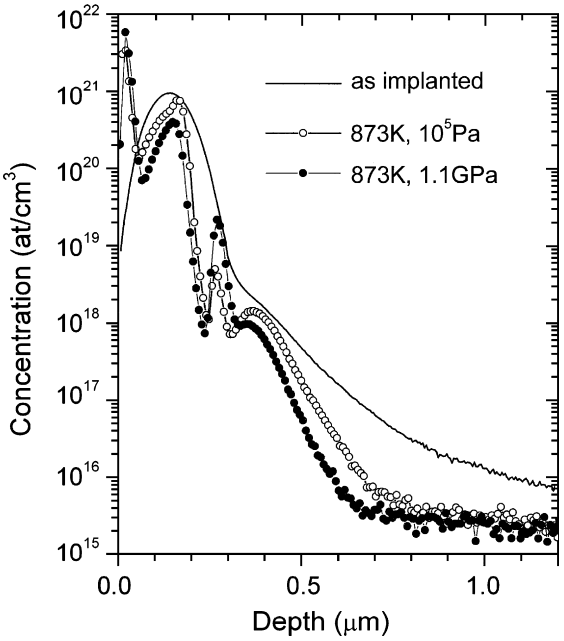

Fig. 3. SIMS depth profiles of ^{55}Mn in BSi:Mn, as-implanted and processed for 1 h at 873 K under 10^5 and 1.1 GPa.

SPER of a-Si and the Mn distribution are strongly dependent on D, HT, HP and on processing time. SPER results in the HT- and t-dependent shift of the a–c interface towards the surface (compare refs. [2,6,7]).

Processing of Si:Mn at ≤670 K for 1 h exerts negligible influence on the shape and position of the Mn concentration profiles [7]; this is obviously related to low mobility of Mn and so to the low SPER rate. As earlier reported [2], also SPER in heavily self-implanted silicon (Si:Si) is minor for the treatments done at 720 K, both under 10^5 Pa and HP. The Si:Si samples are similar in respect of structural damages to presently investigated Si:Mn and so they can be considered as the reference samples.

The depth distribution of implanted Mn atoms in Si:Mn, subsequently processed at 873 K, is strongly dependent on D and, to a lesser extent, on HP (Figs. 2 and 3).

Processing of ASi:Mn ($D = 2 \times 10^{15}$ cm^{-2}) for 1 h at 873 K, both under 10^5 Pa and 1.1 GPa, results in a maximum Mn concentration at ~220 nm depth below the surface; this concentration exhibits a minimum at ~180 nm depth (Fig. 2), probably related to the a–c interface shifted towards the surface.

About 6 times higher energy introduced into the Si lattice in the case of BSi:Mn samples results in more extended damage affecting SPER. Besides the Mn maximum at about 280 nm depth with the corresponding minimum at ~240 nm depth, of possible origin corresponding to that discussed for the ASi:Mn sample, two other maximum–minimum concentration features are observed (Fig. 3). It is known that chemical interaction of implanted Mn with a-Si can occur in Si:Mn, resulting in a synthesis of some Si–Mn compounds, for example $Mn_{11}Si_{19}$ or Mn_4Si_7 [9]. The peak Mn concentration at ~180 nm and the minimum at ~80 nm depths, both located within the region of the highest Mn concentration in as-implanted BSi:Mn (at the level of 10^{21} cm^{-3}), are probably related to a creation of some manganese silicides.

The weak Mn concentration peak at about 0.4 μm from the surface shows evidence of Mn gettering on implantation-induced defects.

In BSi:Mn, enhanced HP applied at 873 K results in a little faster diffusion of Mn towards the surface at the depths shallower than

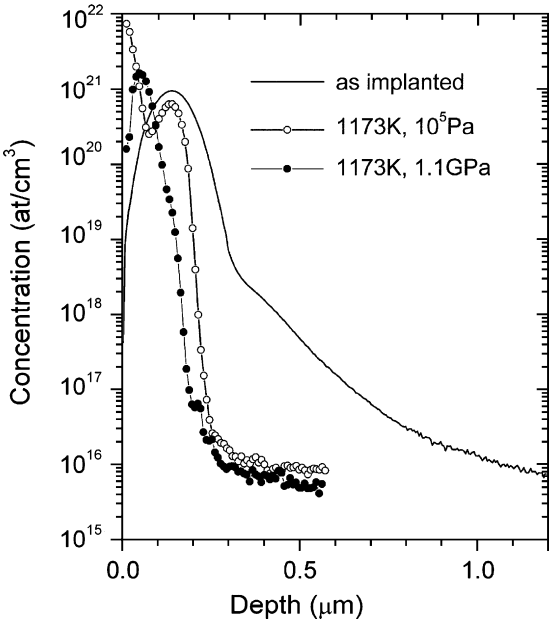

Fig. 4. SIMS depth profiles of ^{55}Mn in BSi:Mn, as-implanted and processed for 1 h at 1173 K under 10^5 and 1.1 GPa.

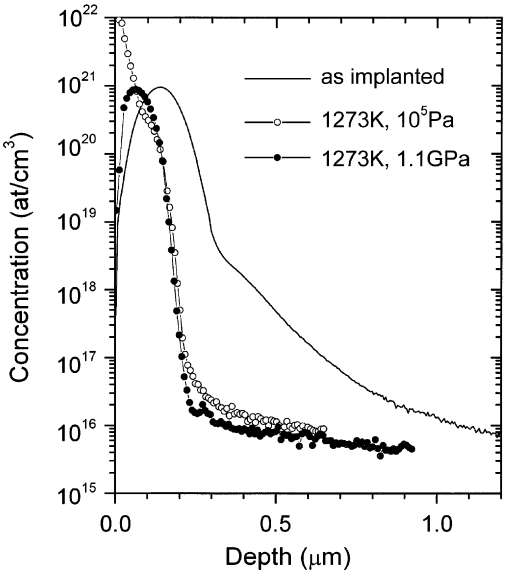

Fig. 6. SIMS depth profiles of ^{55}Mn in BSi:Mn, as implanted and processed for 1 h at 1273 K under 10^5 and 1.1 GPa.

0.2 μm, so within still amorphous silicon (Fig. 3). Both in ASi:Mn and BSi:Mn the tails of Mn distribution shift towards the surface (Figs. 2 and 3).

At higher temperatures SPER expels Mn atoms from the re-growth region as the a–c interface moves towards the surface. This occurs because the equilibrium solubility of Mn in c-Si is low (of about 3×10^{16} cm^{-3} at 1273 K [10]). Mn atoms are accumulated at the a–c interface and, depending on the D value, their concentration reaches a point, at which re-crystallization can no longer push excess Mn out of re-crystallized c-Si. This means that the position of the peaking Mn concentration defines to some extent the a–c interface.

Processing of ASi:Mn at 1173 K for 1 h, both under 10^5 Pa and under 1.1 GPa, results in further shift of the peaking Mn concentration to a 40 nm depth.

Contrary to the case of ASi:Mn, the depth position of the a–c interface in processed BSi:Mn depends strongly on HP (Fig. 4). After processing at 1173 K under 10^5 Pa, the peak Mn concentration and so the a–c interface are placed at about 0.14 μm depth while, after processing under HP, the Mn peak is shifted to about 40 nm depth.

Further increase of processing temperature leads to more complete SPER. The structure of the c-Si layer re-grown from a-Si is worse than that of the Si substrate, indicating directional mosaicity. No distinct effect of HP applied at 1273 K on the perfection of re-grown c-Si has been found by applied X-ray methods (Fig. 5).

The Mn concentration profile in ASi:Mn processed at 1273 K under 1.1 GPa shifts much closer to the Si:Mn surface and exhibits the concentration maximum just below the sample surface.

Processing of BSi:Mn at 1273 K under 1.1 GPa results in the Mn concentration peaking at a depth ~80 nm, while no distinct maximum has been observed after processing under 10^5 Pa (Fig. 6).

Upon annealing, SPER takes place in both A and B-type Si:Mn samples. In the case of ASi:Mn, the near surface damaged layer and the less damaged Si bulk act as the templates/substrates for SPER of a-Si. The near-surface areas of BSi:Mn are much more damaged so SPER of a-Si occurs mainly on the deeper placed, non damaged Si substrate. This means that structural properties of processed ASi:Mn and BSi:Mn are expected to be substantially different; it is evidently the case (observe Figs. 2 and 3).

While experimentally measured concentration maximum in as-implanted samples is located near R_p, processing at 873 K results in D-dependent shift of the Mn maximum into the depth. At ≥ 1173 K the peak Mn concentration moves towards the surface. This shift at ≥1173 K is clearly related to SPER and to out-diffusion of Mn. On the other hand, relatively stable position of the Mn concentra-

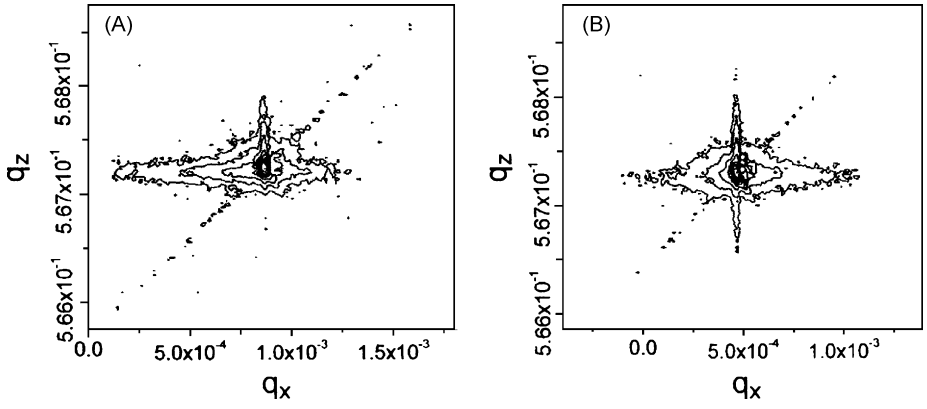

Fig. 5. 0 0 4 XRRSM of ASi:Mn processed for 1 h at 1273 K under 10^5 Pa (A) and 1.1 GPa (B). Axes x and y are in relative reciprocal lattice units (rlu), q_x and q_z.

tion maximum after processing at 1173–1273 K suggests that some manganese silicide is formed.

In BSi:Mn processed at 1173–1273 K, the effective out-diffusion of Mn to the surface increases with uniform stress applied; SPER and the Mn distribution are strongly dependent on HP.

Accounting for substantial differences in behaviour of as-implanted Si:Mn and of Si:Si (related, among others, to metallic ions introduced into Si:Mn, while Si:Si has been prepared [2] by self implantation), it is clear that HP affects SPER in Si:Mn somewhat similar to that in Si:Si. As in Si:Si [2], HP-related transformations of the Si:Mn structure are dependent first of all on the effect of HP on diffusion of implantation-induced point defects. Most vacancies and silicon interstitials recombine during implantation while the remaining ones form complex defects, affecting SPER rather adversely. The presence of Mn, in a concentration quite high at the concentration maximum (typically near R_p), assists in the formation of the mentioned complex defects, among them of manganese silicides.

4. Conclusions

Our results help in understanding the mechanisms of SPER and, in the particular case of Si:Mn, suggest a new route to prepare, by appropriate HT–HP treatment, specific Si–Mn materials belonging to the Diluted Magnetic Semiconductor family. Among other important issues, further extended research on response of the structural and magnetic properties of Si:Mn on the implantation/processing parameters are recommended.

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