

Strain state in Mn-implanted silicon annealed at high temperature

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In this work an influence of thermal annealing of Mn-implanted silicon on strain state of silicon matrix is presented. During post-implantation annealing, nanocrystalline tetragonal Mn_4Si_7 compound is formed. A strong correlation between the size of nanoinclusions and the matrix strain state is detected.

1. Introduction

In recent years, much interest has been devoted to materials called diluted magnetic semiconductors (DMS): mixed crystals based on classic semiconductors, with a controlled fraction of nonmagnetic cations substituted by the magnetic ones [1]. Silicon-based DMS would be the preferred spintronics material due to existing technology used in Si-based microelectronics and wide availability of high quality Si single crystals. Dietl et al. [2] predicted a carrier-mediated ferromagnetism for silicon doped with 5 % Mn. For wide commercial application room-temperature ferromagnetism in DMS is desired. Zhang et al. [3] reported the $Mn_{0.05}Si_{0.95}$ alloy with Curie temperature, T_C , of about 400 K.

Ion implantation is one of the methods utilized to achieve ferromagnetic properties of semiconductors. Ferromagnetic ordering in Mn-implanted Si has been reported recently (e.g. [4-7]). For Si:Mn produced by implantation with Mn^+ doses, $D = 10^{15} - 10^{16} \text{ cm}^{-2}$, at energy, $E = 300 \text{ keV}$, T_C exceeds 400 K after its rapid thermal annealing at 800°C [4]. Randomly distributed Mn atoms play twofold role: promote the formation of local magnetic moment and supply free carriers (holes) which mediate exchange interaction between the local moments). It has been suggested that the ferromagnetic exchange is carrier mediated.

However, due to low solubility of Mn in Si and easy Mn reaction with Si, the formation of manganese silicide in Mn-implanted Si is often observed. It has been found that high-temperature-pressure annealing of Si:Mn produced by implantation results in a creation of Mn_4Si_7 inclusions [8,9]. However, these Mn_4Si_7 nanoinclusions in Si show ferromagnetism with magnetic moment higher than that of the bulk ($T_C \approx 45 \text{ K}$, according Ko et al. [10]). Therefore, the Mn_4Si_7 phase rather cannot be considered as a main source of ferromagnetism at or above room temperature. Our last results indicate on an influence of the Mn_4Si_7/Si interface on magnetic ordering of Mn^+ -implanted silicon [9].

The inclusions formed during post-implantation thermal processing may influence the strain state of the crystals (see, e.g. [11]). The aim of the present work is to determine the influence of the Mn-containing inclusions on the silicon matrix strain state.

2. Experimental

Czochralski and Floating-zone (001)-oriented silicon single crystals were implanted with 160 keV Mn^+ ions to a dose of $1 \times 10^{16} \text{ cm}^{-2}$. Such implantation causes a creation of quasi three-layers structure composed, in sequence, of the damaged near-surface Si layer (thickness $\sim 100 \text{ nm}$), the Mn-implanted Si layer ($\sim 50 \text{ nm}$) and the almost undamaged Si substrate. Maximum concentration of the Mn-implanted ions equal to about 1.2% is observed at the depth of $\sim 140 \text{ nm}$. To modify the defect structure of Si:Mn and rebuild the damaged material, the samples were annealed for 1 h at temperatures up to 800°C under ambient pressure of 10^5 Pa .

The phase composition of polycrystalline layers created during the processing at the near-surface areas was measured using X-ray diffraction techniques and synchrotron radiation. The results presented earlier [8,9] showed that Mn-containing nanoinclusions, identified as the tetragonal Mn_4Si_7 compound, are formed. Using transmission electron microscopy technique as well as by study the slopes of the diffraction rocking curves it has been found that the sizes of the inclusions increase with annealing temperature, whereas their concentration decreases [9].

High-resolution Philips Material Research Diffractometer equipped with a standard laboratory source of $CuK_{\alpha 1}$ radiation was used to study the strain distributions in the silicon matrix. Secondary ion mass spectroscopy (SIMS) depth profiles of Mn were measured using the CAMECA IMS6F spectrometer.

3. Results

Strain distribution in the Si matrix was determined from the analysis of the shape of X-ray diffraction peak. Unsymmetrical shape of the 004 X-ray diffraction peaks

shows on a distribution of the matrix lattice parameter (see Fig. 1 and 2). This effect is the same for Czochralski and Floating-zone Si:Mn samples and disappears after 800°C processing. For this temperature the particle sizes exceed 20 nm [9]. These particles become incoherent in respect to the silicon matrix and so strain disappears (the tensile strain occurs below the 15 nm size). Simultaneously, the SIMS technique showed that the diffusion of Mn ions in effect of temperature processing was insignificant (Figs 3 and 4). It means that there exists a strong correlation between the size of nano-inclusions and the matrix strain state.

Numerical simulation of the X-ray diffraction peaks, using the Epitaxy 4.0 made Panalytical B.V by softwer, has been performed and depth distribution of the Si-matrix strain has been obtained (Fig. 5). The maximum strain appears at the depth corresponding approximately the maximum Mn concentration. Stress connected with the mentioned above Si matrix strain (the Hook law) can result in a creation of the inclusion-related strain, e.g. [11]. Therefore, Mn_4Si_7 inclusions can be deformed in respect to the bulk material. To distinguish this possibility, precise measurements of the lattice constant of inclusions must be performed in future.

4. Conclusions

Using various experimental methods, including synchrotron radiation measurements, correlation between dimensions of Mn_4Si_7 inclusions and strain state of the Si matrix was found. It occurred to be possible to find the critical values of these dimensions for the case they become incoherent in respect to the Si matrix.

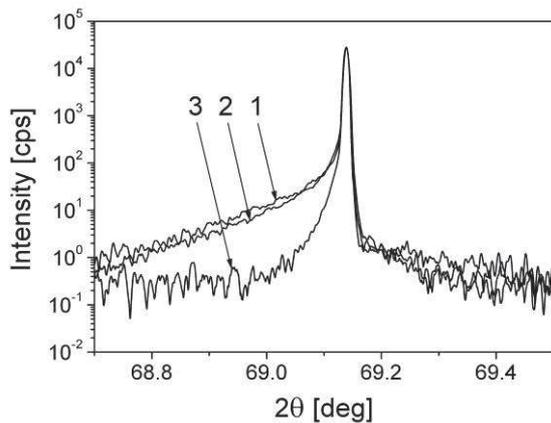


Figure 1. $2\theta/\omega$ X-ray diffraction patterns (004 Si reflection) for Czochralski Si:Mn samples annealed for 1 h at 340°C (1), 600°C (2) and 800°C (3).

Figure 4. SIMS Mn depth profiles for Floating-zone Si:Mn as-implanted sample (1) as well as for samples annealed for 1 h at 340°C (2) and 800°C (3).

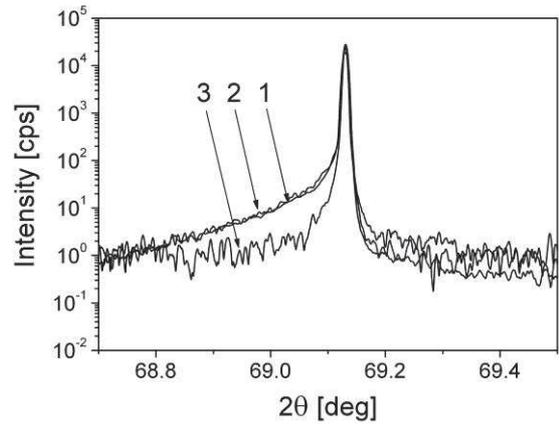


Figure 2. $2\theta/\omega$ X-ray diffraction patterns (004 Si reflection) for Floating-zone Si:Mn samples annealed for 1 h at 340°C (1), 600°C (2) and 800°C (3).

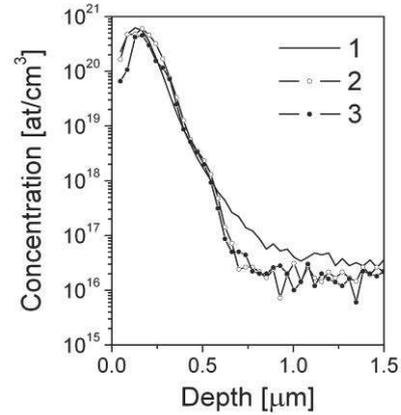
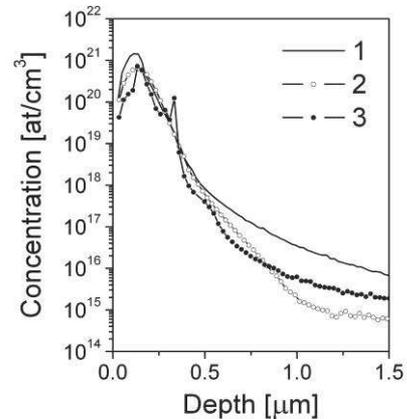


Figure 3. SIMS Mn depth profiles for Czochralski Si:Mn: as-implanted sample (1) as well as for samples annealed for 1 h at 600°C (2) and 800°C (3).



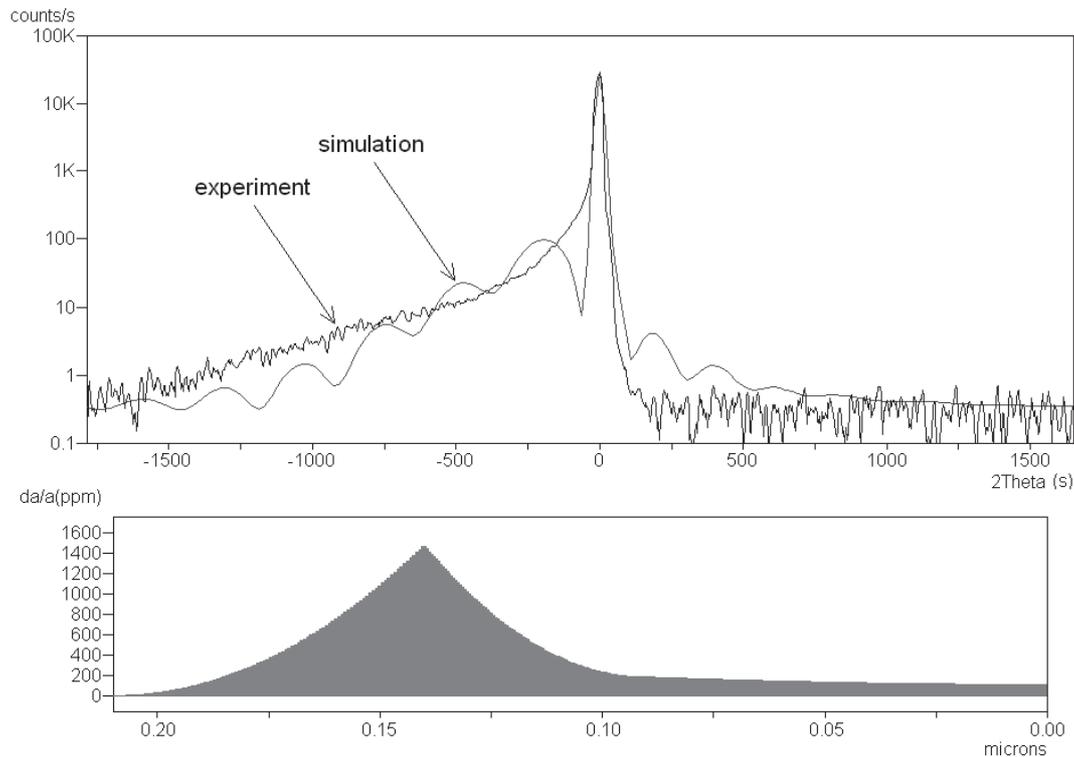


Figure 5. Numerical simulation of $2\theta\omega$ X-ray diffraction pattern (upper) and depth distribution of the Si-matrix strain (lower) for Czochralski Si:Mn sample annealed for 1 h at 340°C .

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