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Magnetic properties of silicon crystals implanted with manganese*

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The influence of thermal treatment on magnetic properties of Si/Mn crystals grown by the Czochralski and by floating zone methods and implanted with Mn^+ ions was studied by the SQUID magnetometry and electron spin resonance. Depending on thermal and hydrostatic pressure annealing conditions, three groups of Si/Mn samples were found: samples with only ferromagnetic phase, samples with ferromagnetic and paramagnetic contributions, and diamagnetic samples. The Curie temperature of ferromagnetic phase exceeds room temperature. The ESR and SQUID measurements suggest that Si/Mn implanted layer is magnetically inhomogeneous.

Key words: *ferromagnetic semiconductor; silicon; implantation*

1. Introduction

Utilizing the spin of electron in semiconductor devices opens new field of potential applications in high-speed and low-power spintronic devices [1, 2]. One of the main research directions in this field concerns ferromagnetic semiconductors created by appropriate magnetic and electrical doping of classical semiconductor materials. Particularly important is the search for ferromagnetism in Si – the most important material of electronic industry – for which theoretical models suggest the carrier concentration induced ferromagnetism to exist above room temperature. Nowadays, numerous groups investigate the magnetic properties of silicon structures doped by magnetic ions, prepared by various evaporation methods [3] or implantation [4, 5]. Recent examination of Si implanted with Mn^+ ions indicated an appearance of ferromagnetic

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phase after implantation process with the estimated Curie temperature over 400 both K in n-type and in p-type materials [4]. The authors suggested that the ferromagnetic exchange is carrier mediated. In this paper, we report on experimental studies of the magnetic properties of silicon crystals implanted with Mn ions and subject to various thermal and hydrostatic pressure treatment regimes.

2. Experimental

The investigated Si/Mn structures were prepared by implantation of Mn^+ ions at energy $E = 160$ keV with the dose $D = 10^{16}$ cm^{-2} into two types of Si crystals. The first group – silicon wafers grown by Czochralski method (CzSi/Mn) – exhibited p-type conductivity with hole concentration $p = 10^{15}$ cm^{-3} and interstitial oxygen concentration $c_{\mathrm{O}} = 9\times10^{17}$ cm^{-3}. The other group of Si crystals, fabricated by floating zone method (FzSi/Mn), was characterized by n-type conductivity with electron concentration $n = 10^{14}$ cm^{-3} and oxygen content $c_{\mathrm{O}} = 1.5\times10^{17}$ cm^{-3}. The implantation process for CzSi crystals was carried out without substrate heating with silicon wafer temperature $T_S \le 340$ K. In the case of FzSi structures, the wafer was heated and the implantation was done at $T_S = 610$ K. Subsequently, the Si/Mn samples were annealed in Ar atmosphere for $t \le 10$ h under hydrostatic pressure $HP \le 1.1$ GPa in a broad temperature range $540 \le T_A \le 1400$ K [6].

The crystal structure of Si/Mn was investigated by X-ray diffraction (reciprocal space mapping, XRRSM) and photoluminescence (PL) methods. The Mn depth profiles were measured by the secondary ion mass spectrometry (SIMS). The carrier concentration on the implanted and on the back (non-implanted) sides was controlled by electrical impedance measurements and calculated based on current–voltage (*I–V)* and capacitance–voltage (*C–V*) characteristics of the Schottky barrier junction Hg–Si.

The temperature and magnetic field dependence of magnetization was studied using a SQUID magnetometer in a broad temperature range (5–300 K) in the magnetic field up to 800 Oe. Only for a few samples, the investigation was performed at higher magnetic fields in order to reach magnetization saturation. For all investigated samples the weak magnetic signal was recorded with the maximum signal detected in Si/Mn about $(5–10)\times10^{-6}$ emu (measurement error equals 5×10^{-7} emu). The temperature and angle dependences of the electron spin resonance (ESR) spectra were measured by an X-band (9.4 GHz) Bruker spectrometer in the temperature range 2–300 K.

3. Results and discussion

Based on the PL measurements and the X-ray diffraction analysis, one may conclude that the crystal structure of CzSi/Mn prepared by implantation at $T < 340$ K is strongly disordered due to atomic displacements after implantation. The crystal structure of FzSi/Mn is more ordered with a well defined layered geometry. The PL measurements of the samples also indicate the presence of numerous point defects and dislocations. The results of SIMS measurements are presented in Fig. 1. Projected range of the distribution of implanted Mn ions equals 140±50 nm with the width of distribution of about 100 nm. The thermal treatment of CzSi/Mn at temperature below 670 K has practically no effect on Mn distribution while the annealing at higher temperature shifts the Mn ions distribution towards the surface (Fig. 1). This Mn redistribution effect only weakly depends on the hydrostatic pressure. After the thermal treatment of FzSi/Mn structures, the profile of Mn distribution in Si wafer practically does not change.

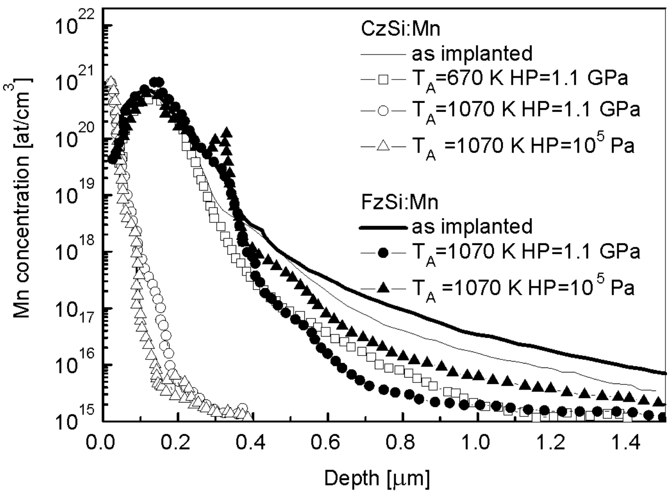

Fig. 1. Depth profiles of Mn in CzSi/Mn and FzSi/Mn samples, as implanted and annealed for 1 h at the temperature and under hydrostatic pressure conditions indicated in the figure

The electrical measurements were performed on implanted and on back sides of CzSi/Mn and FzSi/Mn structures annealed at 720 K for 10 h. Mn^+ implantation produces both donors and acceptors – the implanted CzSi/Mn samples are p-type while FzSi/Mn ones are n-type. After annealing the CzSi/Mn samples exhibiting higher oxygen concentration, a change of the type of conductivity to n-type was found. The carrier concentration on the implanted side is of the order of $n = 10^{16}$–10^{17} cm^{-3} for the CzSi/Mn sample and $n = 10^{14}$–10^{16} cm^{-3} for FzSi/Mn sample. Such a low carrier concentration puts in question the free carrier origin of ferromagnetic coupling between Mn ions in implanted Si/Mn layers. For instance, in the well known ferromagnetic semiconductors, in which ferromagnetic coupling between Mn ions is induced by free carriers ($Pb_{1-x-y}Sn_yMn_xTe$ and $Ga_{1-x}Mn_xAs$) the threshold carrier concentration is about 10^{20} cm^{-3}.

Based on the SQUID magnetization measurements, the Si/Mn samples can be divided into three groups. The samples from the first group exhibit ferromagnetic behaviour with the ferromagnetic hysteresis loop almost temperature independent in a broad temperature range. Magnetization of these samples remains practically constant up to the room temperature, which indicates the Curie temperature exceeding room temperature in these materials (Fig. 2a). Assuming that Mn ions with S = 5/2 magnetic moment create magnetically homogeneous 100 nm thick implanted layer of $Si_{1-x}Mn_x$, the amount of ferromagnetic Mn ions corresponds to x = 0.5 at. %. The magnetic behaviour of the samples from the second group is characterized by the presence of both ferromagnetic and paramagnetic contributions (Fig. 2b). In order to describe the temperature dependence of magnetization, three contributions were taken

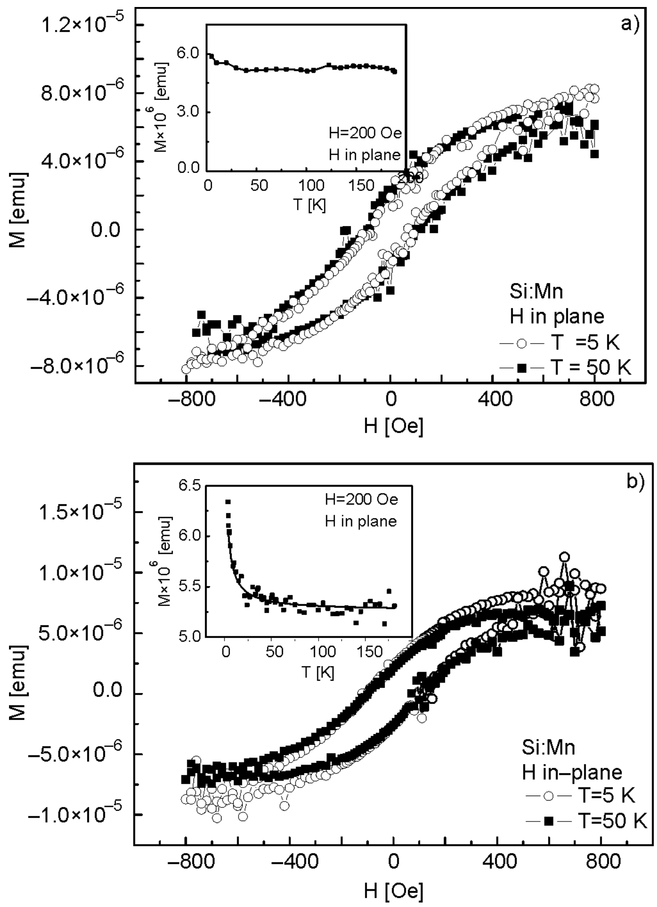

Fig. 2. Ferromagnetic hysteresis loops at various temperatures for samples from the first (a) and the second (b) groups. The insets show the temperature dependence of magnetization. The solid line presents the Curie-Weiss law fit

into account: diamagnetic (Si crystal), as well as paramagnetic and ferromagnetic phases of Si/Mn. Based on the Curie–Weiss law fitting, the amount of paramagnetic Mn ions can be evaluated as corresponding to x = 1.5 at. %. The samples from the third group show diamagnetic properties, which suggests that most of Mn ions are incorporated in Si matrix in a magnetically inactive form. In the case of FzSi/Mn structures, the thermal treatment conditions have been determined for which all samples exhibit the ferromagnetic ordering (275 °C ≤ T_A ≤ 450 °C, other parameters being of lesser importance). For CzSi/Mn structures, reliable establishing of such technological conditions failed. The main conclusion of the thermal treatments is that heating of a silicon wafer during implantation process enables fabrication of a more magnetically predictable structure. Below certain temperature of post growth treatment, the FzSi/Mn structures remain with evident ferromagnetic contribution plus more or less strong paramagnetic contribution. In order to decrease the contribution of ferromagnetism in these structures, higher temperatures during the post growth treatment are needed. In the non-heated CzSi/Mn structure, the magnetic distribution of Mn ions is more chaotic so any thermal treatment conditions cannot guarantee obtaining a Si/Mn structure with ferromagnetic ordering.

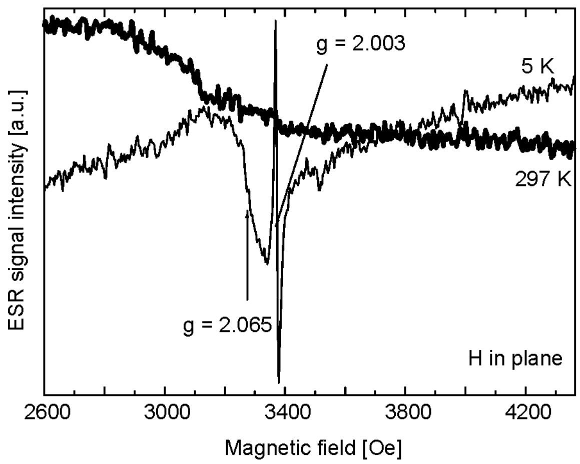

Fig. 3. X-band ESR spectra of FzSi/Mn crystal. The arrows point to two main resonance lines identified by their *g* factors

The ESR measurements revealed in Si/Mn samples at low temperatures the main resonance line with the *g* factor equal 2.003 (Fig. 3). We tentatively assign this very narrow ESR line to unpaired spins of electrons of lattice defects in Si (e.g., dangling bonds) or in SiO_2 [7, 8]. The broader line with the *g* factor equal to 2.065 which also is visible in the ESR spectrum cannot be assigned to single Mn ions but rather to magnetic Mn–Si nanoparticles. As this weak resonance overlaps with background signal from the quartz sample holder, we are unable to make any definite conclusion about Mn-related ESR signal in Si/Mn implanted structures. From the ESR measurements, we can clearly conclude that a small ferromagnetic contribution observed in SQUID measurements does not originate from any ultra thin continuous ferromagnetic layer. The ESR spectra of Si/Mn reveal neither the angular dependence due to shape anisotropy nor temperature dependence characteristic of ferromagnetic resonance. This conclusion supports the idea of Mn–Si nanoparticles enriched with Mn as a microscopic origin of ferromagnetic properties of Si/Mn. Such objects have been observed by TEM investigations of Si implanted with Mn [9] which revealed regions with bands of dislocations and stacking faults along with a variety of Mn-rich nanoparticles and silicides [10].

Additionally, we performed a series of reference magnetic measurements of Si crystals implanted with other magnetic ions (Cr and V) and non-magnetic ions (Si and He). For Si implanted with Si only diamagnetic properties were observed. In the case of magnetic ions implantation, we observed a ferromagnetic behaviour of the investigated samples. Surprisingly, also Si crystals implanted with He ions show a certain small ferromagnetic contribution. This suggests that the possibility of appearance of ferromagnetism may not necessarily be connected with the presence of magnetic ions. Some authors observed the ferromagnetic properties in Si structures without any magnetic ions [11]. They explain the appearance of ferromagnetic ordering by unpaired spins of the dangling bonds. Therefore, the origin of ferromagnetism in Si crystals implanted with Mn^+ ions needs further investigations with a careful examination of possible contamination of Si/Mn structures with magnetic ions during the implantation process.

4. Conclusions

The magnetic properties of Si crystals implanted with Mn were experimentally studied by the SQUID magnetometry and the ESR. The implanted Si/Mn samples can be divided in three groups: samples with dominating ferromagnetic phase (Curie temperature exceeds room temperature), samples with ferromagnetic and paramagnetic phases coexisting and diamagnetic samples. Technological regimes of thermal treatment of FzSi/Mn structures exhibiting the ferromagnetic ordering were determined. The analysis of SQUID and ESR measurements indicate the absence of magnetically homogeneous thin ferromagnetic Si/Mn layer but rather point to the import role of Si-Mn nanoparticles and cooperative effect of unpaired spins of electrons of various crystal defects.

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