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PRESSURE-INDUCED STRUCTURAL TRANSFORMATIONS IN Si:V and Si:V, Mn

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Semiconductors doped with magnetically active atoms are expected to find application in spintronics. Si samples implanted with Mn^+ (Si:Mn) or with V^+ (Si:V) can order magnetically after processing at high temperature (HT) and also under enhanced hydrostatic pressure (HP). This work presents new results on structure-related properties of single crystalline Si implanted at 200 keV with V^+ as well as that co-implanted additionally with Mn^+ ions (Si:V, Mn), with dosages $D_{V+} \le 5\cdot10^{15}$ cm^{-2} and $D_{Mn+} = 1\cdot10^{15}$ cm^{-2}. The samples were processed for 1–5 h at HT ≤ 1270 K under HP ≤ 1.1 GPa. Secondary Ion Mass Spectrometry, Transmission Electron Microscopy, X-ray and related methods were applied for sample characterization. The HT- (HP) treatment affects, among others, solid phase epitaxial re-growth (SPER) of amorphous silicon created at implantation and distribution of implanted species.

Introduction

Most investigations on semiconductors doped with magnetically active atoms, which are expected to be applied as diluted magnetic semiconductors (DMS), are still focused on ferromagnetic Mn-doped III–V semiconductors, such as $Ga_{1-x}Mn_xAs$, and on ZnO and similar oxides doped with transition metals (TM) [1,2].

Recently, Si samples implanted with Mn^+ (Si:Mn) [3] as well as with Cr^+ or V^+ (Si:Cr and Si:V) have been also demonstrated to order magnetically after processing at high temperature (HT) under enhanced hydrostatic pressure (HP) of inert gas ambient [4,5].

The HT- (HP) treatment affects SPER of *a*-Si created at implantation. Specific local ordering near the implanted metal atoms in Si:TM materials (TM = V, Cr or Mn) can be critical with respect to the formation of ferromagnetic ordering [6]. Still, magnetic properties of the as-implanted as well as of processed Si:V, Si:Cr and Si:Mn samples could be related in part to the so called quasi-ferromagnetism reported for Si implanted with non-magnetic species, such as He^+ or Si^+, and processed at relatively low temperatures [7].

This work reports new results concerning structural and related properties of Si:V (implanted dose, $D_{V+} \le 5\cdot10^{15}$ cm^{-2}) as well as of Si:V, Mn ($D_{V+} = 5\cdot10^{15}$ cm^{-2}, $D_{Mn+} = 1\cdot10^{15}$ cm^{-2}), processed at up to 1270 K under HP up to 1.1 GPa.

Experimental

Implantation of $^{51}V^+$ to a dose $D_{V+} \le 5\cdot10^{15}$ cm^{-2} into single crystalline (*c*-Si) Czochralski grown Cz–Si wafers with (001) orientation (to produce Si:V), sometimes followed by $^{55}Mn^+$ implantation (to produce Si:V, Mn), was performed at room temperature at energy $E_{V+,Mn+}$ = 200 keV. The projected range of implanted ions, R_p, was about 170 nm.

The Si:V and Si:V, Mn samples were processed for 1–5 h in Ar atmosphere at up to 1270 K under 10^5 Pa or HP = 1.1 GPa.

The present results concern mostly Si:V prepared by V^+ implantation with $D_{V+} = 5\cdot10^{15}$ cm^{-2} and Si:V, Mn prepared by V^+ implantation with the same dose, then followed by Mn^+ implantation to a dose $1\cdot10^{15}$ cm^{-2}. If not otherwise stated, in what follows just such samples are labelled as Si:V and Si:V, Mn.

The depth distribution of Mn was determined by Secondary Ions Mass Spectrometry (SIMS, Cameca 6F instrument). X-Ray Reciprocal Space Mapping (XRRSM, MRD–PHILIPS diffractometer), Transmission Electron Microscopy (TEM) and photoluminescence (PL, at 10 K, excitation with Ar laser, λ = 488 nm) methods were applied to reveal structure of the samples. Magnetic properties of as implanted Si:V were determined at 5 K using SQUID magnetometer.

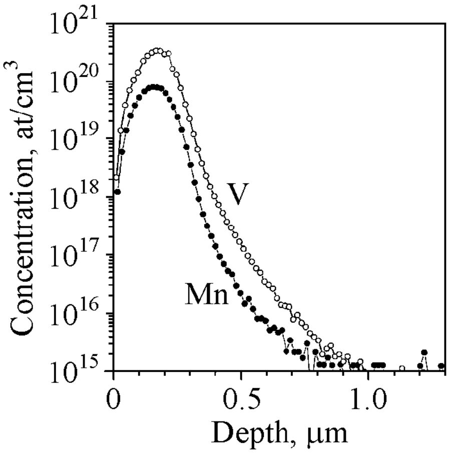
Results and discussion

Heavy implantation of silicon with V^+ produces strongly disordered area near R_p. For the case of E = 200 keV and $D = (1–2)\cdot10^{15}$ cm^{-2}, the total energy introduced during implantation into Si is above the amorphization threshold. So in the case of $D_{V+} \ge 10^{15}$ cm^{-2}, amorphization of Si takes place near R_p with a creation of buried amorphous *a*-Si layer. Subsequent Mn^+ implantation with $D_{\mathrm{Mn}+} = 1 \cdot 10^{15}$ cm^{-2} to produce Si:V, Mn, results in even more complete amorphization.

Depth distributions of V and Mn in as-implanted Si:V, Mn are presented in Fig. 1. Depth distribution of V in Si:V prepared by implantation with $D_{\mathrm{V}+} = 1 \cdot 10^{14}$ cm^{-2} and $D_{\mathrm{V}+} = 1 \cdot 10^{15}$ cm^{-2} is of the same character as that presented in Fig. 1.

After implantation, the *a*-Si layer, enriched in V/Mn up to about 1 at.%, has been formed in Si:V and Si:V, Mn at about 170 nm depth below the surface (Fig. 1).

As seen in Fig. 2, magnetization observed for Si:V prepared by implantation with $D_{\mathrm{V}+}$ in the $1 \cdot 10^{12}$ cm^{-2}–$1 \cdot 10^{15}$ cm^{-2} range, is dominated by the diamagnetism of the silicon substrate. The Si:V ($D_{\mathrm{V}+} = 1 \cdot 10^{15}$ cm^{-2}) sample, processed at 610 K, has been reported to order magnetically with magnetization slightly decreasing with temperature increase, from 5 to 50 K [4].



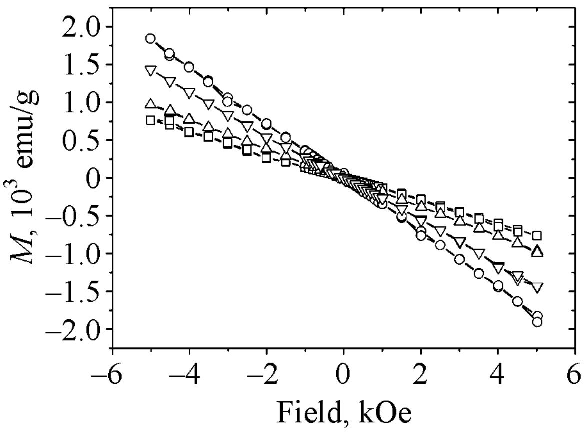


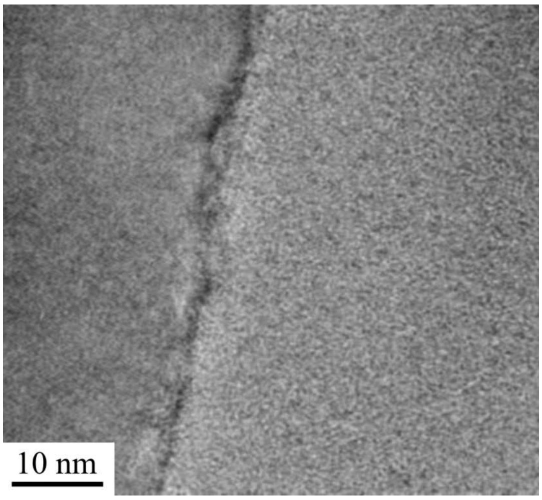
Fig. 1. SIMS depth profiles of Mn and V in as-implanted Si:V, Mn

Fig. 2. Magnetization M versus magnetic field for as-implanted Cz–Si:V ($E_{\mathrm{V}+}$ = 200 keV): –□– – Si:V5 ($D_{\mathrm{V}+} = 10^{12}$ cm^{-2}), –○– – Si:V6 (10^{13}), –△– – Si:V7 (10^{14}), –▽– – Si:V7 (10^{15}). Measurements were made at 5 K

As revealed by TEM, the treatment of Si:V at 610 K results in a partial recovery of the initial crystallographic perfection (Fig. 3). In effect of processing at HT (HP), V and Mn atoms become to be distributed more uniformly through the *a*-Si area, most probably because of enhanced, if compared to that in *c*-Si, diffusivity of Mn and V atoms within *a*-Si.

At high temperatures, the *a*-Si layer is subjected to SPER, dependent on HT, processing time and on HP [4]. In Si:V and Si:V, Mn this results in a movement of the *a*–*c* interface toward the surface [8], detectable through either SIMS measurements (Figs. 4, 5) or cross-sectional TEM (compare Fig. 3).

V atoms are excluded from the re-growth region, as the *a*-Si/*c*-Si interface moves toward the surface, because the solubility of V in crystalline Si is very low [9]. Through this process, a minimum in the V concentration profile was formed in Si:V at about 300 nm below the surface (Fig. 4). The same phenomenon is also



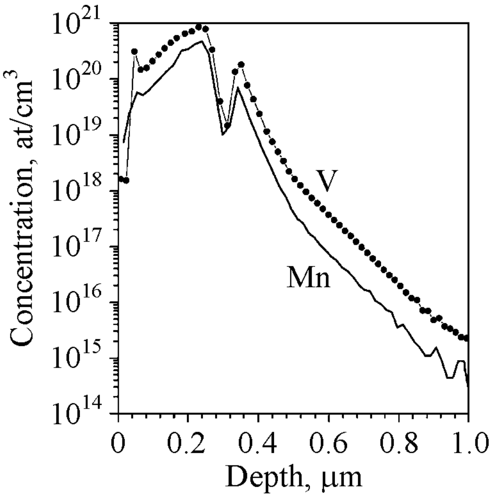


Fig. 3. High-resolution TEM image of Si:V ($D_{V+} = 5 \cdot 10^{15}$ cm^{-2}) processed for 1 h at 610 K under 1.1 GPa. Width of re-growth region (left) equals to about 50 nm

Fig. 4. SIMS depth profiles of Mn and V in Si:V, Mn processed for 5 h at 1070 K under 1.1 GPa

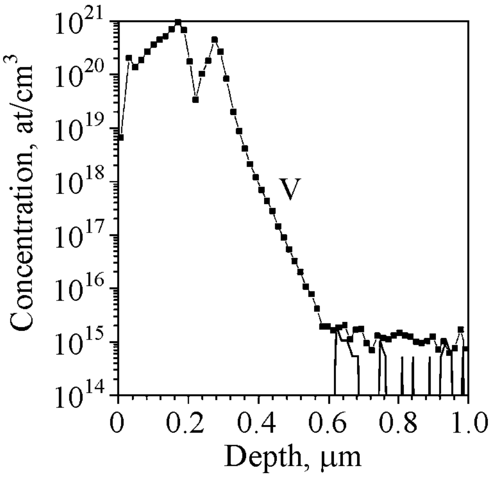


Fig. 5. SIMS depth profile of V in Si:V processed for 5 h at 1270 K under 1.1 GPa

observed for Mn atoms, which are concentrated at the same positions as vanadium. It is important to admit that, in the case of Si:Mn prepared by Mn^+ implantation at 160 keV, $D = 1 \cdot 10^{16}$ cm^{-2}, with substrate temperature, $T_{Si} \leq 340$ K, and processed for 1 h at 1070 K, most Mn atoms were shifted toward the Si surface [3]. This means that, in Si:V, Mn, Mn atoms are gettered at defects produced at SPER. This gettering is related to behavior of implanted vanadium.

As mentioned, excess vanadium is accumulated at the *a*-*c* interface, and the V concentration reaches a point, at which excess V impurity cannot be pushed away. At higher temperatures (HT ≥ 900 K), the *a*-Si layer is converted into the partially polycrystalline state and VSi_2 compound is formed [10]. Enthalpy of the VSi_2 formation equals 3.2 eV, so this silicide remains stable even at 1270 K and so, both in the case of Si:V and Si:V, Mn, it is located almost at the same depth, at about 280 nm below the sample surface (Fig. 5).

The V concentration is peaking also at about 170 nm depth, near R_p (Figs. 4, 5), so within the maximal V concentration induced by implantation itself. This even more pronounced peak seems to be also related to a formation of VSi_2. The similar Mn concentration peak observed in Si:V, Mn processed at 1070 K or 1270 K at this depth can be related to a formation of Mn_4Si_7 [11].

Similarly as in the case of self-implanted silicon, Si:Si [12], processing of Si:V or Si:V, Mn at 1270 K – 10^5 Pa/1.1 GPa does not result in a fully recovered crystallographic perfection of the implantation-damaged areas. This has been stated basing on PL (Fig. 6) and XRRSM (Fig. 7) results. Processing of Si:V, Mn under HP results in an absence of the PL line at about 0.81 eV (Fig. 6,*b*), still clearly detectable after processing under 10^5 Pa (Fig. 6,*a*). Usually this line is associated with the presence of dislocations in single-crystalline Si.

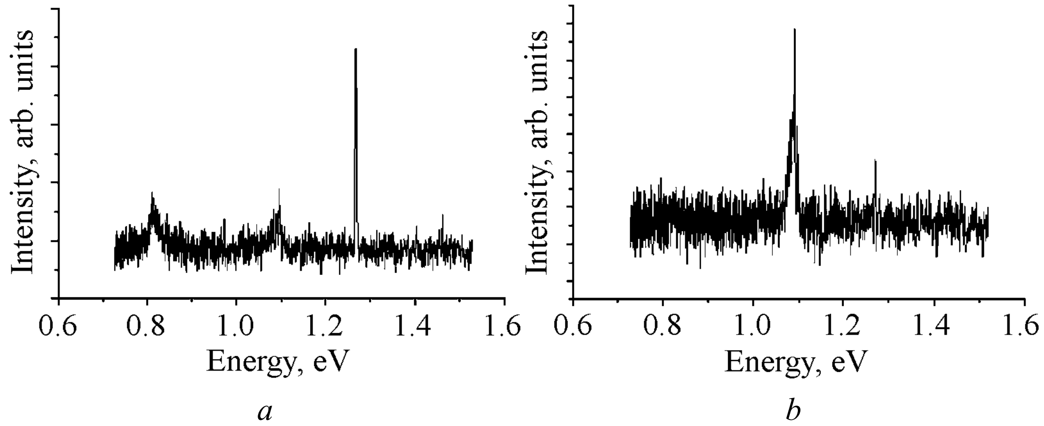


Fig. 6. PL spectra of Si:V, Mn processed for 5 h at 1270 K under 10^5 Pa (*a*) and 1.1 GPa (*b*)

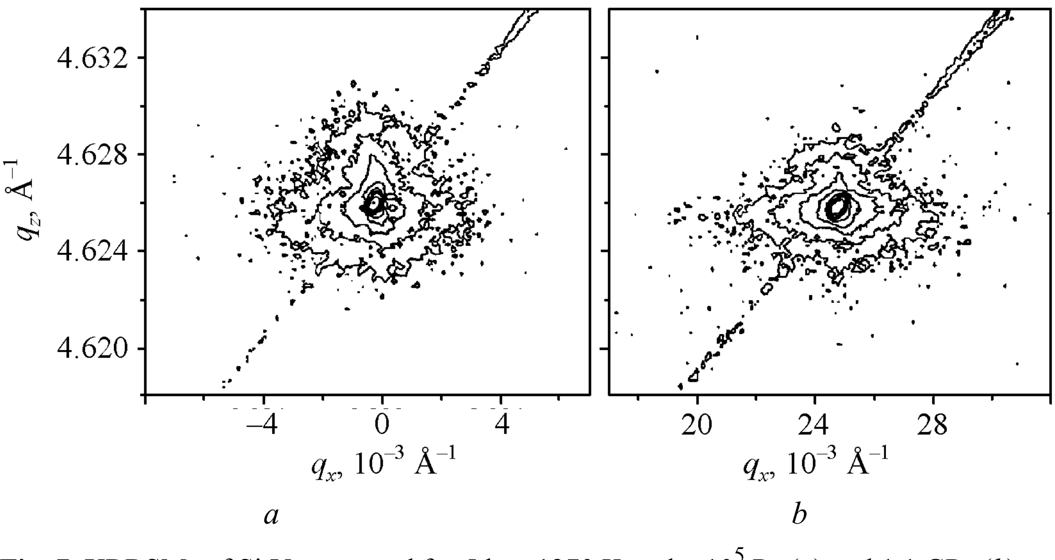


Fig. 7. XRRSMs of Si:V processed for 5 h at 1270 K under 10^5 Pa (*a*) and 1.1 GPa (*b*)

The favourable effect of HP at 1270 K on SPER is confirmed by X-ray mapping. The intensity of diffusively scattered X-rays decreased in the case of Si:V processed at 1270 K under HP. The lattice parameters of *c*-Si, formed under 1.1 GPa by SPER of *a*-Si, were distinctly more uniform (compare Fig. 7,*a*,*b*).

After processing, the structure of Si:V and Si:V, Mn samples (these last with $D_{V+}/D_{Mn+} = 5$), is dependent first of all on the dose of implanted V^+ and on temperature of processing. Enhanced pressure of Ar affects SPER and results in the improved structure of re-crystallized *a*-Si, most probably due to the effect of HP on diffusivity of implantation-induced point and related defects [12].

Local ordering near the implanted atoms in Si:TM materials (TM = V and/or Mn) is critical for magnetic ordering. This ordering is also related to quasi-ferromagnetism, detected in silicon implanted with non-magnetic atoms [7,9].

Conclusions

Our report presents the compositional and structural properties of single-crystalline silicon implanted with medium dosage of vanadium (vanadium + manganese) ions and processed at up to 1270 K, also under enhanced pressure, up to 1.1 GPa.

Understanding the mechanisms of SPER under HP and so of magnetic ordering in ion implanted Si-based materials, of the creation of specific crystalline magnetically ordered phases and of the origin of quasi-ferromagnetism demands further research.

One can hope that new Si–V and Si–V, Mn materials belonging to the DMS family will be developed.

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1. *H. Ono*, Physica **B376–377**, 19 (2006).
2. *O.D. Jayakumar, I.K. Gopalakrishnan, S.K. Kulshrestha*, Physica **B381**, 194 (2006).
3. *A. Misiuk, B. Surma, J. Bak-Misiuk, A. Barcz, W. Jung, W. Osinniy, A. Shalimov*, Mater. Sci. Semicond. Process. **9**, 270 (2006).
4. *A. Misiuk, L. Chow, A. Barcz, B. Surma, J. Bak-Misiuk, P. Romanowski, W. Osinniy, F. Salman, G. Chai, M. Prujszczyk, A. Trojan*, in: High Purity Silicon 9, C.L. Claeys, R. Falster, M. Watanabe, P. Stallhofer (Eds.), ISBN 1-56677-504-3 (2006), p. 481–489.
5. *A. Misiuk, A. Barcz, L. Chow, B. Surma, J. Bak-Misiuk, M. Prujszczyk*, Solid State Phen. **131–133**, 375 (2008).
6. *A. Wolska, K. Lawniczak-Jablonska, M. Klepka, M.S. Walczak, A. Misiuk*, Phys. Rev. **B75,** 113201 (2007).
7. *T. Dubroca, J. Hack, R.E. Hummel, A. Angerhofer*, Appl. Phys. Lett. **88**, 182504 (2006).
8. *P. Zhang, F. Stevie, R. Vanfleet, R. Needlakantan, M. Klimov, D. Zhou, L. Chow*, J. Appl. Phys. **96**, 1053 (2004).
9. *L. Chow, J.C. Gonzales-Pons, E. del Barco, R. Vanfleet, A. Misiuk, A. Barcz, E.S. Choi, G. Chai*, in: Magnetic Materials, International Conference on Magnetic Materi-

als (ICMM-2007), A. Ghoshray, B. Bandyopadhyay (Eds.), American Institute of Physics (2008), p. 248–251.
10. *S.P. Murarka*, Silicides for VLSI Applications, Academic Press, New York (1983).
11. *J. Bak-Misiuk, E. Dynowska, P. Romanowski, A. Shalimov, A. Misiuk, S. Kret, P. Dluzewski, J. Domagala, W. Caliebe, J. Dabrowski, M. Prujszczyk*, Solid State Phen. **131–133**, 327 (2008).
12. *A. Misiuk, B. Surma, J. Bak-Misiuk*, Solid State Phen. **108–109**, 351 (2005).