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Properties of Si:Cr Annealed under Enhanced Stress Conditions

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Abstract. The effect of hydrostatic argon pressure equal to 10^5 Pa and 1.1 GPa applied to processing at up to 1270 K (HT) of Si:Cr samples prepared by Cr^+ implantation (dose $1x10^{15}$ cm^{-2}, 200 keV) into (001) oriented Czochralski silicon, has been investigated by Secondary Ion Mass Spectrometry, photoluminescence, X-ray and SQUID methods.

Cr^+ implantation at this energy and dosage produces amorphous silicon (a-Si) near the implanted ions range. Solid phase epitaxial re-growth (SPER) of a-Si takes place at HT. The Cr profile does not depend markedly on HP applied during processing at 723 K. Si:Cr processed at up to 723 K indicates magnetic ordering. Annealing under 10^5 Pa at 873 K, 1070 K and 1270 K results in a marked diffusion of Cr toward the sample surface. In the case of processing under 1.1 GPa this diffusion is less pronounced, SPER of a-Si is retarded and the a-Si/Si interface becomes enriched with Cr. The Cr concentration in Si:Cr sample processed at 1270 K under 1.1 GPa forms two distinct maxima, the deeper one at 0.35 μm depth.

Introduction

Transition metal impurities in silicon affect adversely the reliability and performance of integrated circuits. This is one of the reasons for the current interest in metal diffusion at high temperatures (HT) in single crystalline Si grown by Czochralski method (Cz-Si) [1].

In 2001 it has been shown that GaN films implanted with Mn possess ferromagnetic ordering at up to 250 K [2]. Later, the behaviour of single crystalline silicon implanted with manganese (Si:Mn) has been reported [3], showing ferromagnetic ordering up to 400 K. Recently, it has been demonstrated that processing of Si:Mn samples under enhanced hydrostatic pressure (HP) results in the formation of Si:Mn with unusual properties, also including magnetic ordering [4].

Annealing of Cz-Si implanted with chromium (Si:Cr) at 570 – 1270 K under atmospheric pressure (10^5 Pa) results in the solid phase epitaxial re-growth (SPER) of amorphous Si (a-Si) produced at implantation [5]. Magnetic ordering in silicon implanted with vanadium (Si:V) and processed at enhanced temperatures under 10^5 Pa and under HP as well in as - implanted Si:Cr has been reported recently [6].

These observations motivated us to check the effect of HP applied at processing of the Si:Cr samples on their structural properties.

Experimental

$^{52}Cr^{+}$ ions were implanted (at energy 200 keV, at room temperature) into (001) p – type boron doped Cz-Si wafers to a dose $1x10^{15}$ cm^{-2}.

Cz-Si contained the oxygen and carbon admixtures, with the concentrations, respectively, ≈ $8x10^{17}$ cm^{-3} and ≤ $2x10^{16}$ cm^{-3}. Projected range (R_p) of implanted $^{52}Cr^{+}$ was about 0.2 μm.

The Si:Cr samples were processed in argon atmosphere for 1 h at up to 1270 K under 10^5 Pa and enhanced pressure (HP) equal to 1.1 GPa.

The distribution of Cr in the as - implanted and processed samples was investigated by Secondary Ions Mass Spectrometry (SIMS, Cameca IMS 6F) using O^+ ions for sputtering. Photoluminescence (PL, excited at 6 K by Ar laser, wavelength λ = 488 nm) and X-ray Reciprocal Space Mapping (XRRSM) were used to determine the sample microstructure. SQUID measurements were applied to check the samples for magnetic ordering.

Results and discussion

Cr^+ implantation produces an amorphous silicon (a-Si) layer up to the implanted ions range (R_p). The PL spectrum of the as - implanted sample is featureless confirming practically complete amorphisation of the Si:Cr near – surface layer (at PL probing silicon is excited by the Ar laser up to ~ 0.25 μm depth).

Processing of the Si:Cr samples at 723 K, both under 10^5 Pa and 1.1 GPa, does not affect markedly the Cr profile. A small Cr concentration peak formed at a depth of about 0.28 μm, near the projected range of implanted Cr^+ (Fig. 1), indicates the movement of the amorphous / crystalline (a/c) interface due to the solid phase epitaxial re-growth [5]. No evidence of the HP effect on the Cr diffusivity in silicon is detected for such low processing temperature. The Si:Cr samples, as - implanted [6] and processed at 723 K indicate hysteresis loops evidencing ferromagnetic ordering (Fig. 2).

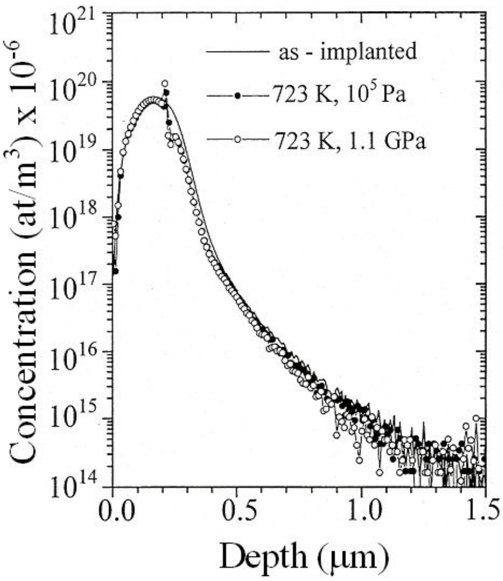

Fig. 1. SIMS depth profiles of Cr in Si:Cr, as-implanted and processed at 723 K under 10^5 Pa and 1.1 GPa.

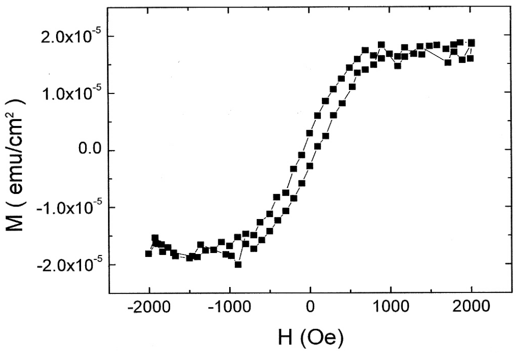

Fig. 2. Magnetization versus magnetic field measured at 5 K for Si:Cr processed for 1 h at 723 K under 1.1 GPa.

Distinct SPER of a-Si takes place at ≥ 873 K (Fig. 3). Maximal Cr concentration at about 0.28 μm depth corresponds to the a/c interface in as-implanted Si:Cr. The concentration minimum at 0.25 μm shows the effect of SPER. Apparently the solubility of Cr in silicon is low. As the a/c interface moves toward the surface, the over - saturated Cr impurities have been "snowplowed" towards the surface and form a concentration minimum.

From X-ray measurements it has been deduced that, after processing for 1 h at 873 K both under 10^5 Pa and 1.1 GPa, the very top, only partially re-crystallized layer of Si:Cr (composed of a-Si in the as-implanted sample) is of about 0.25 μm thickness (compare [6]).

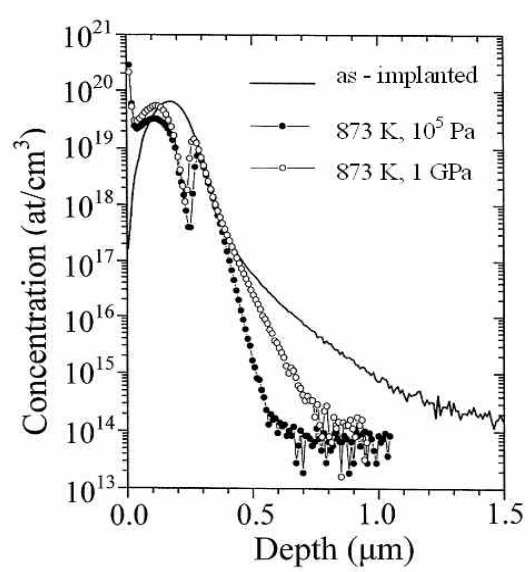

Fig. 3. SIMS depth profiles of Cr in Si:Cr, as-implanted (reference) and processed at 873 K under 10^5 Pa and 1.0 GPa.

The maximum concentration of Cr (at about 0.2 μm depth in the as-implanted samples, Figs 1, 3) shifts toward the Si surface after processing at 873 K (Fig. 3). The Cr concentration profile at the areas deeper then 0.3 μm is strongly dependent on HP (Fig. 3), evidencing, most probably, retarded Cr diffusivity under compressive stress.

As evidenced by appearance of the PL peak near 1.1 eV, related to the interband transitions in crystalline Si, substantial part of a-Si:Cr re-crystallizes due to processing at 873 K for 1 h, both under 10^5 Pa and HP (Fig. 4). Better resolved PL lines, especially near 1.1 eV, detected for the Si:Cr sample processed at 873 K under HP, seem to show that its crystallographic perfection is improving with HP.

It is important to note that, contrary to the case of self–implanted silicon [7], no dislocation–related PL is detected after processing of Si:Cr at 873 K. Si:Cr samples processed at 1070 K indicate the Cr concentration profiles as well as the PL spectra similar to the these ones observed after processing at 873 K (compare Figs 4 and 5).

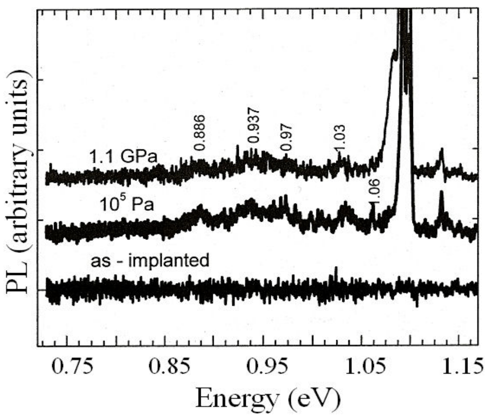

Fig. 4. PL spectra of Si:Cr samples, as-implanted (reference) and processed at 873 K under 10^5 Pa and 1.1 GPa.

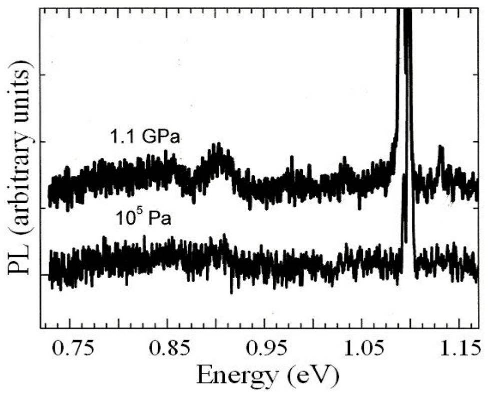

Fig. 5. PL spectra of Si:Cr samples processed at 1070 K under 10^5 Pa and 1.1 GPa.

As follows from SIMS measurements, annealing of the Si:Cr sample at 1270 K under 10^5 Pa results in almost full segregation of Cr to the narrow near–surface layer (Fig. 6).
It has been suggested [5] that the Cr impurity is trapped by the defects within a-Si. At about 1200 K the Cr – trap complexes are dissociated and most Cr atoms are diffusing toward the surface.

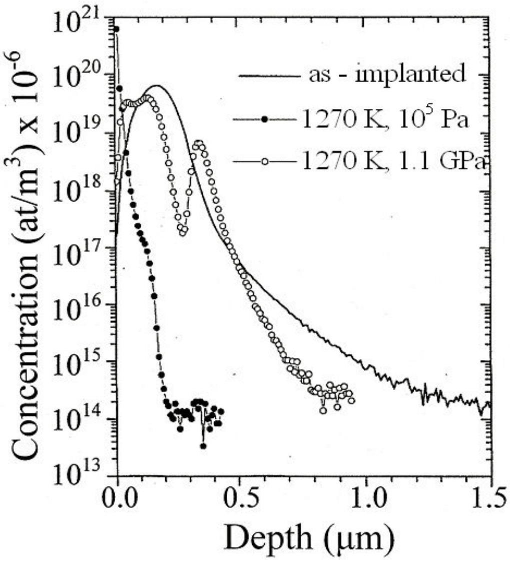

Fig. 6. SIMS depth profiles of Cr in Si:Cr, as-implanted (reference) and processed at 1270 K under 10^5 Pa and 1.1 GPa.

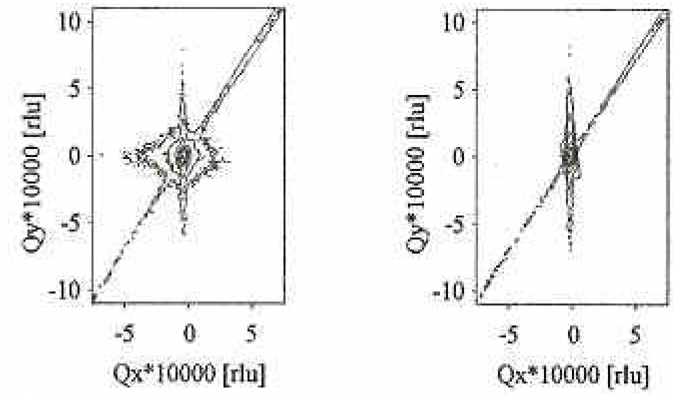

Fig. 7. XRRSMs of Si:Cr processed at 1270 K under 10^5 Pa (left) and 1.1 GPa (right).

In accordance with [5], at 1270 K practically all defect complexes (also the these ones related to the so called end – of – range defects, EOR) are dissolved and just it is the reason for almost complete shift of Cr toward the surface.

Contrary to the case of annealing under 10^5 Pa, processing at 1270 K under HP results in specific conservation of the Cr distribution reached at lower HT (the presence of the concentration maximum at about 0.35 μm depth, compare Figs 6 and 3). This suggest that the EOR – related Cr – containing complexes are stable under HP or / and specific non - soluble Cr clusters are formed at these conditions.

As earlier reported [1], the re-crystallization of a-Si can be considered as complete for the Si:Cr sample annealed for 0.5 h at 1273 K under 10^5 Pa. However, as detected by XRRSM (Fig. 7, left), the Si:Cr sample annealed at 1270 K under 10^5 Pa indicates diffuse scattering of X-rays of rather high intensity, confirming still non complete SPER of the near - surface layer disturbed at implantation and / or the presence of some crystallographic defects.

The PL spectrum (Fig. 8) of that Si:Cr sample, processed for 1 h at 1270 K under 10^5 Pa, indicates only very weak PL near 1.1 eV.

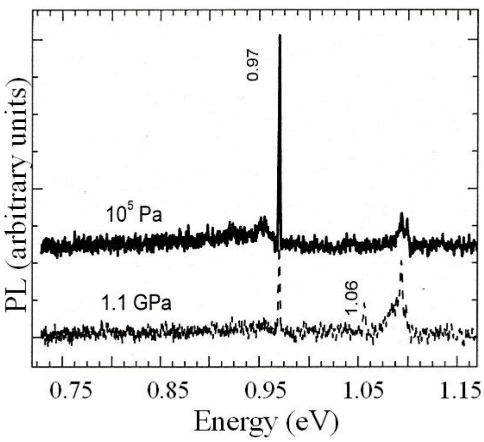

Fig. 8. PL spectra of Si:Cr processed at 1270 K under 10^5 Pa and 1.1 GPa.

One possible explanation of this rather un–expected observation (strong PL at 1.1 eV is detectable in the case of perfect single crystalline silicon and so in the case of completed re-crystallization of a-Si) is the formation at about 1270 K of specific chromium - containing clusters exhibiting strong non - radiative recombination activity and so quenching PL.

The PL spectrum of the same Si:Cr sample but processed under HP exhibits evidently broadened, while still weak PL band near 1.1 eV. One can speculate that this can be related to the presence of non – uniform stress created e.g. by Cr – containing clusters. On the other hand, much weakened X-ray diffuse scattering detected for Si:Cr after processing under 1.1 GPa (Fig. 7) confirms high perfection of its crystallographic ordering and so practically completed SPER. As reported earlier [7], HP applied at annealing of self-implanted silicon affects strongly SPER of a-Si and promotes its re-crystallization at high temperatures.

The origin of sharp PL at 0.97 eV (Fig. 8) is not clear at this moment; it has been suggested [8] that this PL peak (the so called G1 line) originated from the presence of C_s – Si – C_i complexes (C_s and C_i mean carbon in the substitutional and interstitial positions, respectively).

Conclusions

Processing of the Si:Cr samples at up to 1270 K under enhanced hydrostatic pressure modifies markedly solid phase epitaxial re-growth of amorphous silicon produced at implantation and affects the depth distribution of implanted metallic atoms. This means that high temperature – pressure processing can assist in producing specific structures [9] indicating unusual spatial distribution of implanted atoms.

Accounting for recently reported magnetic ordering in Si:V and Si:Mn processed under HT - HP [4, 6, 10], our results suggest a new route to prepare the specific silicon – based materials belonging to the Diluted Magnetic Semiconductor family.

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