Solid State Phenomena Vols. 178-179 (2011) pp 35-40

doi:10.4028/www.scientific.net/SSP.178-179.35

Impact of Hydrostatic Pressure Applied at Annealing on Homogeneity of Si-Ge Single Crystals

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Keywords: Si-Ge, structural properties, annealing, hydrostatic pressure, homogeneity

Abstract. Creation and transformation of defects in single crystalline (001) oriented Si-Ge with about 5.6 at. % Ge content, containing oxygen interstitials, O_i's, at $9x10^{17}cm^{-3}$ level, were investigated, after processing for 5 h at up to 1400 K (HT) under Ar pressure to 1.1 GPa (HP), by X-ray, synchrotron, infrared and photoluminescence methods. To create nucleation centres for O_i's precipitation, some samples were pre-annealed for 10 h at 1000 K under 10^5 Pa. HT-HP treatment at 1230/1400 K results in improved sample homogeneity and crystallographic perfection. HT-HP induced changes in Si-Ge are related mainly to HP-stimulated diffusivity of Ge.

1. Introduction

Czochralski growth of bulk Si-Ge single crystals containing a few atomic % of Ge results usually in non-uniform distribution of Ge in single crystalline Si-Ge rods, both along the growth and radial directions [1, 2]. Growth striations and cellular structures are observed frequently.

Si-Ge single crystals contain agglomerates of Ge atoms and almost uniformly distributed oxygen interstitials, O_i's, these last as the main impurity [2, 3]. Micro inhomogeneity in the Ge distribution is highly undesirable in respect of Si-Ge application in micro-(opto-) electronics.

Processing of Czochralski Si-Ge with a Ge content of 1.4 and 2.6 at. % at enhanced temperature (HT, up to 1400 K) has been reported [3] to result in marked changes of defect structure and in improved sample homogeneity, especially if performed under enhanced hydrostatic pressure (HP).

The creation and transformation of defects in Czochralski-grown Si-Ge with about 5.6 at. % Ge content are now investigated in more detail, also after processing at HT ≤1400 K under HP.

2. Experimental

The p-type (hole concentration ≈$1.3x10^{15}$ cm^{-3}) single crystalline (001) oriented Si-Ge samples of 8x6x(0.5-2) mm^3 dimension, containing about 5.6 at. % of Ge, with O_i's concentration, c_o=$9x10^{17}$ cm^{-3}, were cut from Czochralski grown Si-Ge rods.

To create nucleation centres for precipitation of O_i's, some Si-Ge samples were pre-annealed for 10 h at 1000 K under 10^5 Pa. Next the samples were processed in Ar atmosphere for 5 h at 1230 K and 1400 K under 10^5 Pa (atmospheric pressure) and HP=1.1 GPa.

The structure of Si-Ge samples was investigated by conventional X-ray diffractometry (to record reciprocal space maps, XRRSM's, and to determine lattice parameter, a) as well as by synchrotron methods at HASYLAB DESY to register white beam section, projection and monochromatic beam topographs and to determine Full Width at Half Maximum, FWHM, of the local rocking curves, RC's, recorded using 50x50 μm^2 narrow beam for the 004 reflections with λ=0.1115 nm radiation. Fourier Transform Infrared Spectroscopy, FTIR, was applied to determine the presence of interstitial oxygen (the conversion factor equal to $2.45x10^{17}$ cm^{-3} was used). Photoluminescence, PL, spectra of some samples were also determined at 10 K using Ar laser excitation (λ=488 nm).

3. Results and discussion

The below reported results concern the as grown samples (considered as the reference) and the ones processed under HP at 1230/1400 K. As it has been stated earlier [3], just such processing induced especially strong effect on evolution of the defect structure of Si-Ge.

The presence of Ge in Si-Ge results in strong quenching of PL, related to interband transitions. For example, intensity of the B(TO) peaks at about 1.09 eV decreased for about 25 times when Ge content increased from 1.5 % in the reference sample to 5.6 % (Fig. 1). This effect is probably related to the non-radiative transitions at non-uniformly distributed Ge-enriched clusters (compare Fig. 2).

Segregation of germanium leads also to the scattered lattice parameter values measured perpendicularly to the Si-Ge rod axis (Fig. 2) and to appearance of growth bands detectable in the as grown Si-Ge samples as well as in the ones subjected to the HT-HP treatment (Fig. 3).

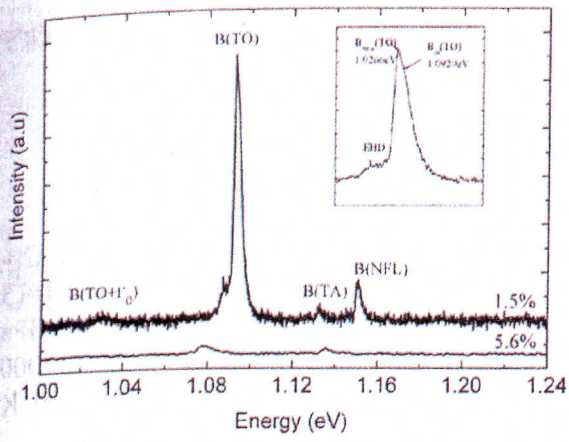

Fig. 1. PL spectra of Cz-$Si_{0.944}Ge_{0.056}$ (bottom) and Cz-$Si_{0.985}Ge_{0.015}$ (reference, top) samples within 1.00-1.24 eV range. B(TO) - transverse optic phonon replica of exciton bound with boron (TO replica of exciton bound with boron), B(NFL) - zero phonon line of exciton bound with boron, B(TA) - transverse acoustic phonon replica of exciton bound with boron (TA replica of exciton bound with boron), TO+Γ_0 – means TO and Γ_0 (phonon at Γ_0 point) replica of exciton bound with boron, EHD -electron hole droplet.

Beside the segregation-related bands, small dislocations and oxygen-related precipitates are detectable at the section and monochromatic beam topographs, especially near the sample surface (Figs 3 and 4).

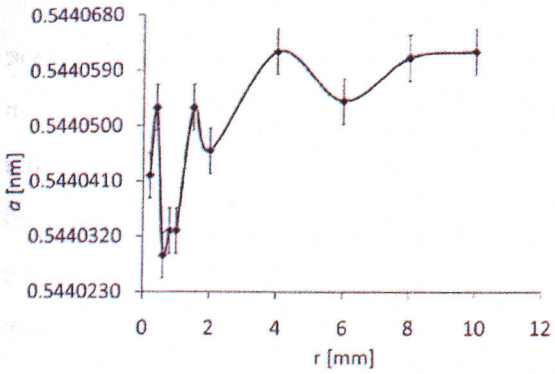

Fig. 2. Lattice parameter *a* at 293 K of as grown Cz-$Si_{0.958}Ge_{0.042}$ measured along sample radius, *r*.

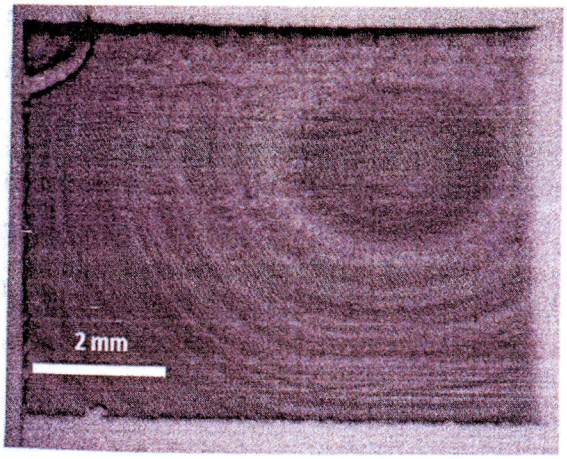

Fig. 3. White beam projection topograph of Cz-$Si_{0.944}Ge_{0.056}$ sample processed at 1230 K under 1.1 GPa.

Annealing at 1230 K results in HP-dependent decrease of FWHM, from 15 arcsec for the as grown sample, to 13 arcsec after processing under 10^5 Pa, and to 6 arcsec after processing for 5 h at 1230 K under 1.1 GPa (see the caption of Fig. 4). It indicates on the HP-dependent improvement of the overall crystallographic perfection. The sample pre-annealed at 1000 K under 10^5 Pa and

subsequently processed at 1230 K under 1.1 GPa, indicates, however, FWHM=11 arcsec. It can be interpreted as an indication of the worsened crystallographic perfection, related to O_i's precipitation.

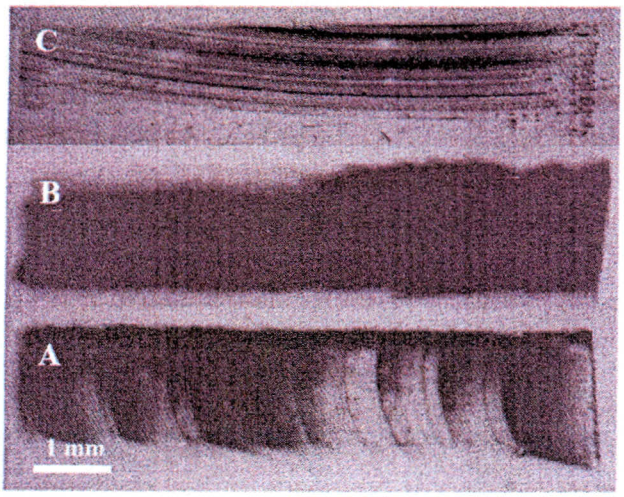

Fig. 4. Monochromatic beam topographs of Cz-$Si_{0.944}Ge_{0.056}$ samples: A–as grown (FWHM=15 arcsec); B–processed at 1230 K under 1.1 GPa (FWHM=6 arcsec); C-processed for 10 h at 1000 K under 10^5 Pa and, subsequently, at 1400 K under 1.1 GPa (FWHM=25 arcsec).

This hypothesis was confirmed by IR measurements (not presented): absorption at 1107 cm^{-1} (evidencing the presence of O_i's) decreased for about 10 % for this sample in comparison to absorption of as grown Si-Ge and of Si-Ge one-stage processed at 1230 K. XRRSM of Si-Ge processed at 1230 K under 10^5 Pa indicates on the crystallographic perfection worsened in comparison to that for as grown Si-Ge (Fig. 5). However, the treatment at the same temperature but under HP produces evidently more perfect sample (compare Fig. 6A and Fig. 5). This HP-induced improvement of sample perfection after the treatment under 1.1 GPa concerns even the Si-Ge sample pre-annealed at 1000 K and so containing numerous defects related to oxygen precipitation (Fig. 6B).

Accounting for the reported dependence of the RC's width and shape on the crystalline perfection [3, 4], one can consider the above observations as an indication of the improved crystallographic perfection of Si-Ge after processing at 1230 K, especially under HP.

Processing of Si-Ge at 1400 K also leads to substantial changes in the defect structure as seen in XRRSM's and synchrotron topographs. While the white beam topographs do not indicate substantial differences, the monochromatic beam ones confirm the treatment-dependent structure (Fig. 4C). Similarly as in the case of processing at 1230 K, the FWHM value of the 004 reflection occurred to be especially sensitive for the treatment conditions at 1400 K. And so FWHM of Si-Ge processed at 1400 K under 10^5 Pa equals to 9 arcsec while, after the treatment under 1.1 GPa, to 6 arcsec only.

Pre-annealing at 1000 K and subsequent processing under 1.1 GPa resulted, however, in much wider FWHM, equal to 25 arcsec (see the caption of Fig. 4).

XRRSM of the Si-Ge sample processed at 1400 K under 10^5 Pa indicates on the worsened crystallographic perfection (Fig. 7A) in comparison to that for as grown Si-Ge (Fig. 5A).

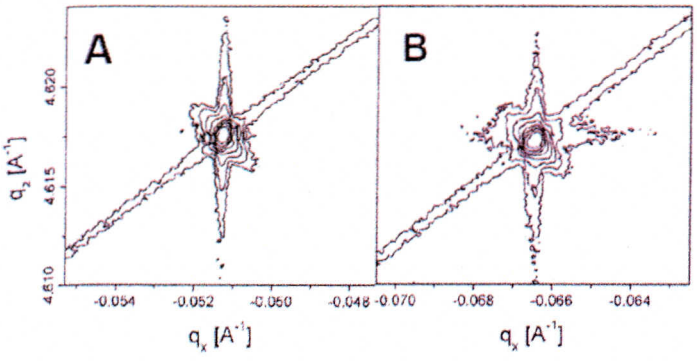

Fig. 5. XRRSM's of Cz-$Si_{0.944}Ge_{0.056}$ samples: A – as grown; B – processed at 1230 K under 10^5 Pa. Axes are marked in reciprocal lattice units (rlu).

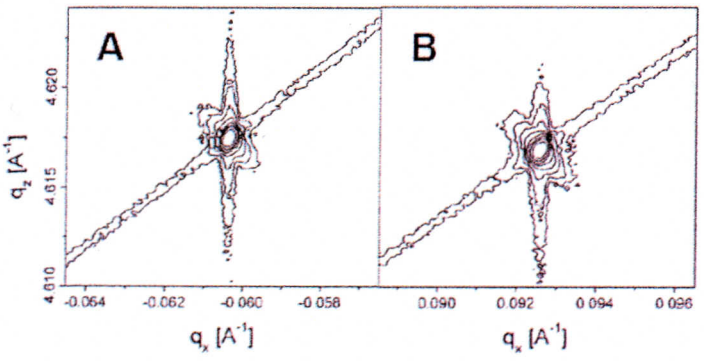

Fig. 6. XRRSM's of Cz-$Si_{0.944}Ge_{0.056}$ samples: A–processed at 1230 K under 1.1 GPa; B–processed for 10 h at 1000 K under 10^5 Pa and, subsequently, at 1230 K under 1.1 GPa. Axes are marked in reciprocal lattice units (rlu).

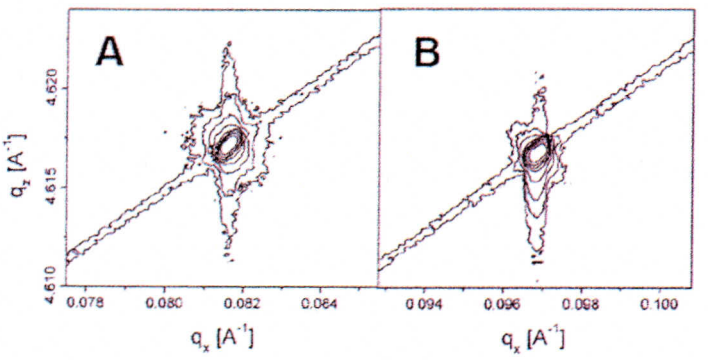

Fig. 7. XRRSM's of Cz-$Si_{0.944}Ge_{0.056}$ samples processed at 1400 K under 10^5 Pa (A) and 1.1 GPa (B). Axes are marked in reciprocal lattice units (rlu).

Similarly as in the case of Si-Ge treated at 1230 K, processing at 1400 K under 1.1 GPa results in the improved structure (Fig. 7). Contrary to the case of processing at 1230 K, the HP-induced improvement of the perfection of the samples pre-annealed at 1000 K was not observed. One can consider this last effect as resulting from massive O_i's precipitation at 1400 K. IR measurements evidence that substantial part of O_i's seems to be transformed, in effect of processing at 1400 K, into oxide precipitates of different shapes, also of these revealing IR absorption at about 1032 nm (related to the presence of needle-like precipitates [5]).

Processing of Si-Ge at 1230 / 1400 K under 10^5 Pa / HP exerts complex effects on the defect structure, related, among other factors, to:

- pressure-stimulated inter-diffusion of silicon and germanium [6] and so to dissolution of Ge-enriched, also nano-dimensional areas in the Si-Ge matrix, and

- precipitation/transformation of interstitial oxygen with a creation of nano-dimensional clusters composed of sub-stoichiometric silicon dioxide.

Diffusivity of Si and Ge is increased at HT, especially under HP (the desirable effect) while oxygen interstitials are clustering so "new" structural defects are formed (the undesirable effect).

4. Conclusions

HT-HP processing of Czochralski grown Si-Ge results in stimulated inter-diffusion of silicon and germanium but also in clustering of oxygen interstitials. Dissolution of nano-dimensional Ge-enriched clusters in the Si-Ge matrix is dependent on temperature, pressure and annealing time as well as on precipitation of interstitial oxygen. The last process is concomitant with a creation of nano-dimensional clusters composed of substoichiometric silicon dioxide. Processing of Si-Ge assists in healing of initially present inhomogeneity in the Ge distribution. While partial healing of structural imperfections and improved homogeneity of the Ge distribution are useful in respect of improved homogeneity, clustering of oxygen interstitials can be considered rather as non-desirable.

In view of important role of Si-Ge in modern microelectronics and optoelectronics, determination of the effect of high temperature–pressure on its structure deserves future research.

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