Vol. **114** (2008) *ACTA PHYSICA POLONICA A* No. 2

Proceedings of the 7-th National Meeting of Synchrotron Radiation Users

Revealing the Defects Introduced in N- or Ge-doped Cz-Si by γ Irradiation and High Temperature–High Pressure Treatment

K. Wieteska[a], A. Misiuk[b], W. Wierzchowski[c], J. Bąk-Misiuk[d], P. Romanowski[d], B. Surma[c], I. Capan[e], D. Yang[f], A. Shalimov[d], W. Graeff[g] and M. Prujszczyk[b]

[a]Institute of Atomic Energy, 05-400 Otwock, Świerk, Poland
[b]Institute of Electron Technology, al. Lotników 32/46, 02-668 Warsaw, Poland
[c]Institute of Electronic Materials Technology
Wólczyńska 133, 01-919 Warsaw, Poland
[d]Institute of Physics, PAS, al. Lotników 32/46, 02-668 Warsaw, Poland
[e]Materials Physics, Rudjer Boskovic Institute, 10000 Zagreb, Croatia
[f]State Key Laboratory of Silicon Materials, Zhenjiang University
Hangzhou 310027, China
[g]HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany

Effect of processing under high hydrostatic pressure (= 1.1 GPa), applied at 1270 K, on Czochralski grown silicon with interstitial oxygen content (c_{O}) up to 1.1×10^{18} cm^{-3}, admixed with N or Ge (Si–N, $c_{\mathrm{N}} \leq 1.2 \times 10^{15}$ cm^{-3}, or Si–Ge, $c_{\mathrm{Ge}} \approx 7 \times 10^{17}$ cm^{-3}, respectively), pre-annealed at up to 1400 K and next irradiated with γ-rays (dose, D up to 2530 Mrad, at energy $E = 1.2$ MeV), was investigated by high resolution X-ray diffraction, Fourier transform infrared spectroscopy, and synchrotron topography. Processing of γ-irradiated Si–N and Si–Ge under high pressure leads to stimulated precipitation of oxygen at the nucleation sites created by irradiation. It means that radiation history of Si–N and Si–Ge can be revealed by appropriate high temperature–high pressure processing.

PACS numbers: 61.05.c–, 61.72.–y, 61.82.–d

1. Introduction

Annealing of oxygen-containing Czochralski grown silicon (Cz-Si) results in defect structure changes due to creation of SiO_{2-x} precipitates formed from interstitial oxygen (O_i), with a concentration, c_O, up to about 1.5×10^{17} cm^{-3}. The presence of substitutional N or Ge atoms in Cz-Si (in what follows such N- or Ge-doped Cz-Si samples are denominated as Si–N or Si–Ge) can suppress creation of oxygen precipitates during annealing (see e.g. [1]).

Irradiation with γ-rays, electrons or neutrons affects the structure of Cz-Si due to creation of interstitials, vacancies and vacancy-related complexes. When Cz-Si is irradiated with the mentioned species of sufficiently high energy, the so-called Frenkel pairs consisting of Si self-interstitials (Si_i) and vacancies (V) are generated. Such defects are annihilated in part already during irradiation. The vacancies and interstitials which have survived annihilation can interact with other dopants, among which the most abundant are O_i's and can act as stronger attractors. In this way vacancy–oxygen (V–O) complexes as well as their clusters are created in the irradiated Cz-Si. In the case of irradiation with γ-rays or electrons, the irradiation induced structural changes are rather weak [2, 3]. However, subsequent processing of irradiated Cz-Si at sufficiently high temperature (HT) causes massive precipitation of oxygen interstitials on nucleation centres (NC's) produced at irradiation, especially in the case of processing performed under enhanced hydrostatic pressure of inert ambient (HP) [2–5]. Such a high temperature treatment under HP has indeed been suggested as a method for revealing the irradiation induced effects in Cz-Si [3].

The aim of this paper was to check the effect of N and Ge admixtures, present in γ-irradiated Si–N and Si–Ge samples on their radiation hardness. As suggested earlier for Cz-Si [3], the radiation hardness of Si–N and Si–Ge with respect to the creation of thermally induced structural defects is investigated after appropriate HT–HP processing. In order to remove the NC's initially present in as-grown Si–N and Si–Ge (which are activated under HP in view of the subsequent oxygen precipitation [6]), prior to γ-irradiation the Si–N and Si–Ge samples were subjected to pre-annealing at 550–1400 K, also under HP. Our intention was to exhaust the initially existing NC's with respect to the precipitation of O_i's so that the newly created γ-induced NC's could be distinguished from the ones present in the as-grown samples.

2. Experimental

Si–N and Si–Ge samples with dimension of about $14 \times 6 \times 2$ mm^3 cut from [001]-oriented Cz-Si rods, doped either with nitrogen ($c_O \approx 1.1 \times 10^{18}$ cm^{-3}, $c_N \leq 1.2 \times 10^{15}$ cm^{-3}) or germanium ($c_O \approx 6.5 \times 10^{17}$ cm^{-3}, $c_{Ge} \approx 7 \times 10^{17}$ cm^{-3}) were investigated in this study. In order to remove NC's originating from as-grown structural irregularities, the as-grown samples were subjected to HT–HP pre-treatments for 5 h at 550–1400 K under HP up to 1.1 GPa. Then the pre-treated samples were irradiated with γ-rays of energy $E = 1.2$ MeV (from a ^{60}Co source) with the dose D up to 2350 Mrad.

The post-irradiation treatment was performed at similar temperature/pressure conditions as the pre-irradiation one. Non-doped reference Cz-Si crystals, not irradiated and similarly treated, were also examined.

The samples were investigated by Fourier transform infrared spectroscopy (FTIR) as well as conventional X-ray and synchrotron methods.

The synchrotron X-ray diffraction measurements were performed at the E2 and F1 experimental stations in HASYLAB. In the present case the basic method was the Bragg-case section topography, realised using a narrow slit of 5 mm, which allowed to detect the presence of small and not well-resolved inclusions and to evaluate the sample perfection better than other X-ray methods. The method provided a high sensitivity, due to formation of various interference patterns, also sensitive to small inclusions. The other important advantage was the possibility to evaluate the depth location of particular defects, as the most intense direct contrast is formed in the vicinity of direct beam intersecting the sample.

An important complementary method was the back-reflection projection topography, where a wide beam (8×1 mm^2) provided images of large areas of the samples. It enabled revealing of defects from near-surface regions of the depth up to 200 μm, although the method is less sensitive than section topography, as the interference effects are smeared. Still, a relatively small glancing angle of 5° could provide a high sensitivity of the back-reflection method.

X-ray high-resolution diffraction investigation with a standard source were also carried out using MRD-PHILIPS diffractometer in the double and triple axis configurations. Reciprocal space maps for the (004) reflections were registered. The defect structure was determined from the X-ray diffuse scattering data near the Bragg reflection point [7]. Simulation of reciprocal space maps was performed using the kinematical theory of X-ray diffraction [8]. The maps of reciprocal space near the 004 reflection were recorded to study the symmetry of X-ray diffuse scattering.

3. Results and discussion

It has been found earlier [3] that γ irradiation can generate NC's for the formation of oxygen precipitates at HT, while the presence of nitrogen or germanium usually moderates this process. As seen in Fig. 1, the O_i content (c_O) in the samples subjected to pre-annealing depends on pre-annealing temperature and, generally, decreases with HT. As a result of the pre-annealing procedure (for 5 h) oxygen precipitates are formed on NC's created during the sample growth. Subsequent irradiation with γ-rays creates additional irradiation-induced NC's which, during processing at 1270 K, serve as the cores for further precipitation of O_i's. This effect is most pronounced in the case of the samples pre-annealed at 1400 K and subsequently γ-irradiated.

The defects due to HT–HP treatment and γ irradiation are practically invisible in the Si–N samples contrary to the Si:Ge ones, as may be seen in the

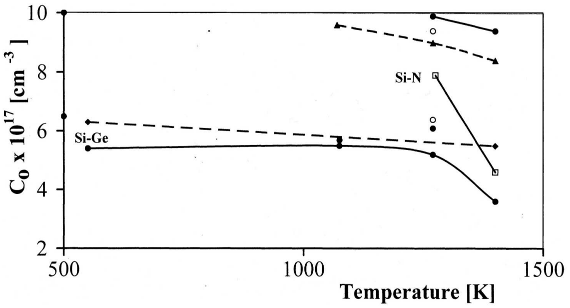

Fig. 1. Dependence of c_O on pre-annealing temperature for Si–N and Si–Ge samples, pre-annealed for 5 h and then subjected to γ-irradiation and processing for 5 h at 1270 K. Upper dashed line: Si–N after pre-annealing for 5 h under 10^5 Pa ($\circ$) or under 1.1 GPa (▲); upper solid lines: Si–N pre-annealed, then γ-irradiated and finally processed under 10^5 Pa ($\bullet$) under 1.1 GPa ($\square$); lower dashed line: Si–Ge after pre-annealing for 5 h under 1.1 GPa (◆); lower solid line: Si–Ge pre-annealed, then γ-irradiated and finally processed for 5 h at 1270 K under 1.1 GPa ($\bullet$).

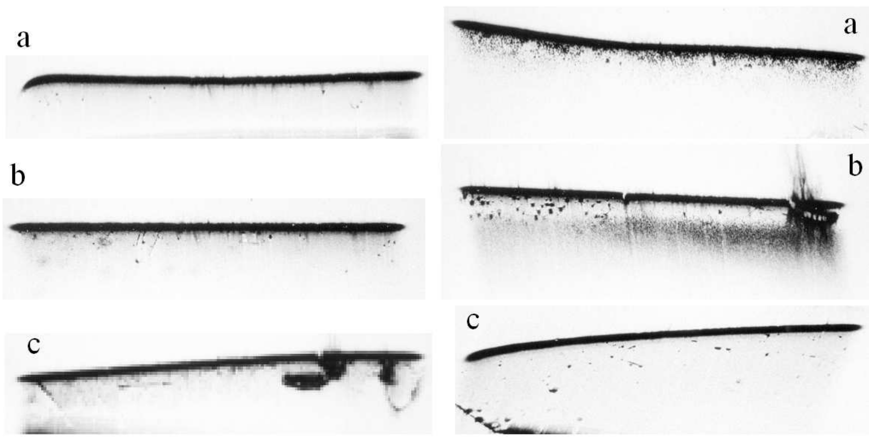

Fig. 2. Bragg case synchrotron white beam section topographs. Left column: Si–N samples, as-grown ((a) and (b)) or pre-treated at 1270 K for 5 h under 1.1 GPa (c), irradiated with γ-rays (D = 2530 Mrad) and subsequently processed for 5 h at 1270 K under 10^5 Pa ((a), (c)), or under 1.1 GPa (b); right column: Si–Ge samples, as-grown (a), pre-treated for 5 h at 1400 K under 10^5 Pa (b) or 1.1 GPa (c), irradiated with γ-rays (D = 2530 Mrad) and subsequently processed for 5 h at 1230 K under 105 Pa (c) or under 1.1 GPa ((a) and (b)).

synchrotron white beam section and projection topographs (Figs. 2 and 3). A set of section topographs of the similarly treated reference crystal (Fig. 4) provides the most significant effects. The defects generated by the treatment appear mainly as a tiny grain structure (Fig. 4a, c) damping the interference effects expected for

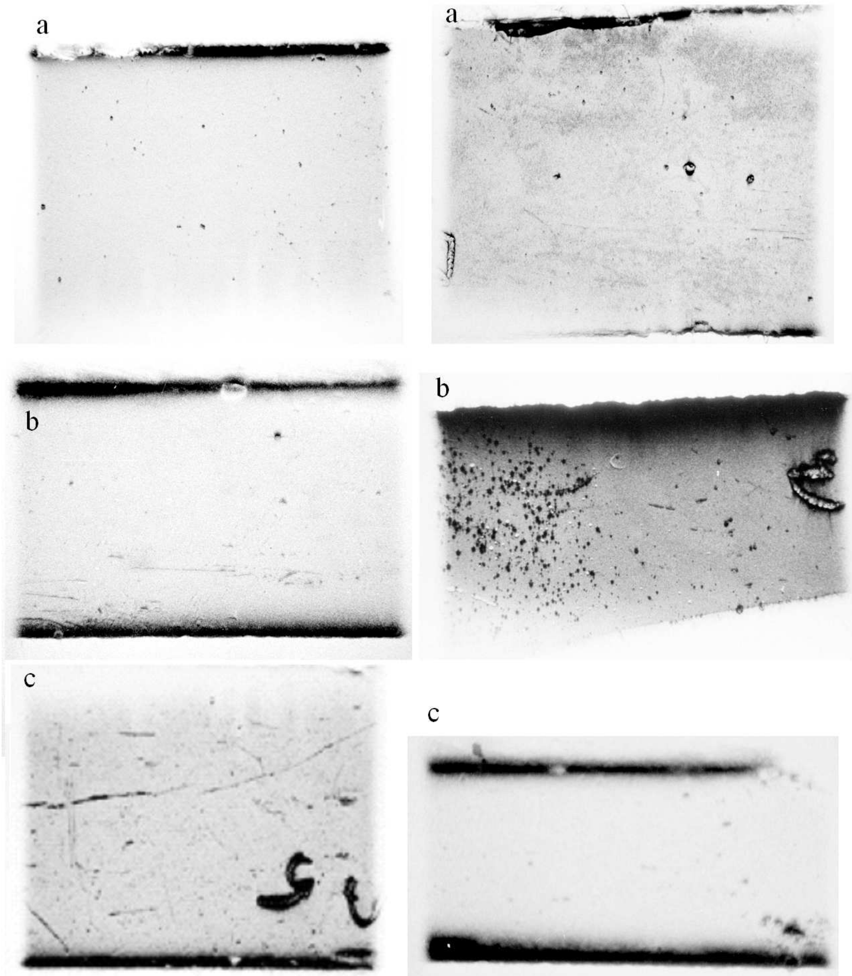

Fig. 3. Bragg case synchrotron white beam projection topographs of the same samples as in Fig. 2 (see its captions for details).

a perfect crystal. The topograph in Fig. 4b indicates that larger defects were created in the near-surface region but a bigger concentration of smaller defects was present deeper in the sample. They are less visible in the Si–Ge samples shown in Fig. 2 as well as in the non-doped and not irradiated sample of Fig. 4a.

In some cases we also observed larger individual contrasts (see in Fig. 4d, but also Fig. 2a, b). However, in the last case of Si–Ge crystals they are partly due to some dislocations present in the as-grown sample. When the initial treatment was performed at up to 1270 K, the effects of irradiation and of the HP–HT treatments were not very distinct, and they were similar for different samples. In the case of the highest temperature applied during the pre-irradiation treatment (1400 K)

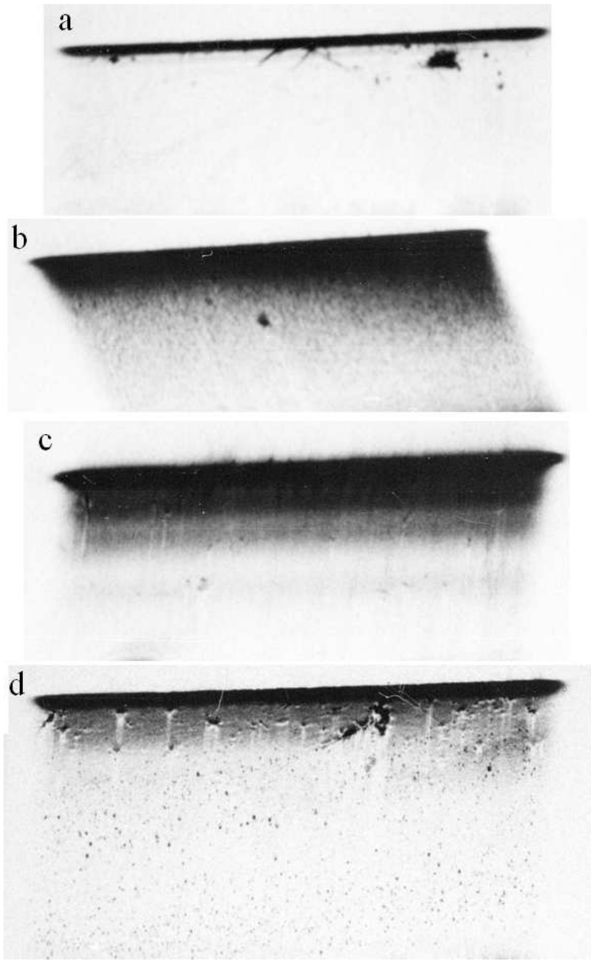

Fig. 4. Bragg case synchrotron white beam section topographs of the non-doped reference Cz-Si sample (as-grown, ((a) and (c)) and of a γ-irradiated one ($D = 1000$ Mrad, (b) and (d)) processed for 5 h under 1.1 GPa at 1270 K (c) or at 1400 K (d).

we observed formation of characteristic inclusions. They were usually of lower concentration in germanium doped samples than in the non-doped ones (Figs. 2 and 4). The observed effects are related to the enhanced radiation hardness of Cz-Si doped with germanium or nitrogen in comparison to that of non-doped material (cf. [1]).

The results obtained by high-resolution X-ray diffractometry are presented in Figs. 5 and 6. The Si:N samples did not exhibit diffuse scattering (Fig. 5a) which means that the defect structure remained unchanged after γ irradiation and the HT–HP treatment, confirming the results obtained by synchrotron topography. A very marked effect was found, however, for the Si–Ge samples (Fig. 5b).

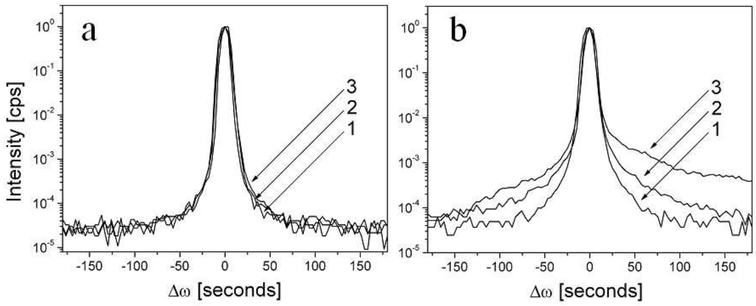

Fig. 5. Rocking curves of Si–N (a) and Si–Ge (b) samples measured in triple axis configuration: (1) as-grown, (2) pre-annealed at 1400 K for 5 h under 10.7 GPa or (3) under 10^5 Pa, irradiated with γ-rays ($D = 2530$ Mrad) and subsequently processed at 1270 K under 10^5 Pa (2) or 1.1 GPa (1, 3).

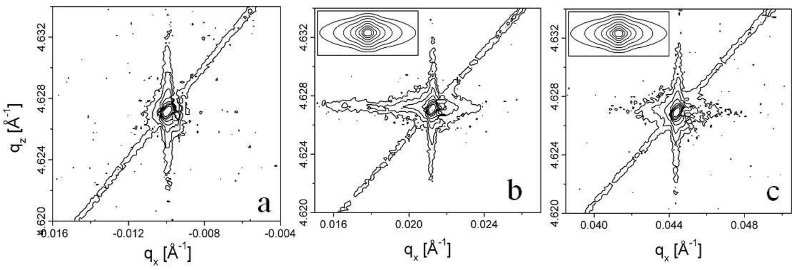

Fig. 6. Reciprocal space maps of Si–Ge samples: (a) as-grown (not thermally pre-treated); (b) pre-treated at 1400 K for 5 h under 10.7 GPa; (c) pre-annealed at 1400 K for 5 h under 10^5 Pa, irradiated with γ-rays ($D = 2530$ Mrad) and subsequently processed for 5 h at 1270 K under 10^5 Pa (b) or 1.1 GPa ((a), (c)). Axes are marked in $\lambda/2d$ units, where λ — wavelength and d — interplanar distance. Insets: kinematical diffraction simulations.

The diffuse scattering intensity, related to the presence of defects, is the highest for the Si–Ge sample pre-annealed at 1400 K under 10^5 Pa, γ irradiated and finally treated at 1230 K under 1.1 GPa. X-ray diffuse scattering originates from the defects seen also in the topographs (Fig. 2b). The lower density of defects detected in the topographs of Figs. 2a and c results in the lower diffuse scattering intensity (Fig. 5a).

The reciprocal space maps of Si–Ge samples are presented in Fig. 6. From their simulations (see the insets in Fig. 6b and c) it follows that processing at 1270 K results in creation of defects of the weak type [8], e.g. dislocation loops or stacking faults. These results correspond well with the results of topographic investigations shown in Figs. 2 and 3.

Therefore, irradiation and the HT–HP treatment resulted in the changed defect structure of Si–Ge, as seen from the increased intensity of X-ray diffuse scattering and/or from additional contrast in X-ray topographs. However, additional defects were not detected in the similarly treated Si–N samples.

When Cz-Si is irradiated with energetic particles (or photons) of sufficiently high energy, self-interstitials and vacancies (the Frenkel pairs) are generated. These defects annihilate partly already during irradiation. The remaining vacancies (V's) and interstitials (Si_i's) interact with impurities present in Cz-Si, among which O_i's are the strongest attractors, and form V–O clusters of vacancies and interstitials as well as larger V_xO_y type clusters, the latter especially in the case of neutron irradiated Si.

4. Conclusions

Processing of irradiated Czochralski silicon at 720–1400 K under enhanced hydrostatic pressure of ambience contributes to revealing the irradiation induced defects in non-doped Cz-Si. Appropriate HT–HP processing results in a specific enlargement of these defects, which is helpful in their recognition. One can hope to use this phenomenon in radiation detection and dosimetry, e.g. for space and military applications.

In the case of pre-treated Si–N, in which the c_{O} value is especially strongly affected by γ-irradiation and subsequent HT–HP treatment, no marked effect of this γ-induced oxygen precipitation is observed by synchrotron reflection topography and high-resolution diffractometric method. It means that oxygen precipitates are very small, and their presence does not affect the crystallographic perfection in a way detectable by the X-ray methods applied. On the other hand, similar processing of Si–Ge samples results in much larger clearly detectable strain fields related to oxygen precipitates, in spite of much lower amount of oxygen precipitates (Δc_{O} is equal approximately to 3×10^{17} cm^{-3} in the case of Si–Ge pre-annealed at 1400 K while $\Delta c_{\mathrm{O}} \approx 5.5 \times 10^{17}$ cm^{-3} in the similarly processed Si–N). It means that γ-induced nucleation centres in both cases are different to some extent.

References

[1] D. Yang, *Phys. Status Solidi A* **202**, 931 (2005).

[2] A. Misiuk, B. Surma, C.A. Londos, J. Bak-Misiuk, W. Wierzchowski, K. Wieteska, W. Graeff, *Phys. Status Solidi C* **2**, 1812 (2005).

[3] A. Misiuk, B. Surma, J. Bak-Misiuk, C.A. Londos, P. Vagovic, I. Kovacevic, B. Pivac, W. Jung, M. Prujszczyk, *Radiat. Measur.* **42**, 688 (2007).

[4] A. Misiuk, B. Surma, J. Bak-Misiuk, I.V. Antonova, S.A. Smagulova, *Vacuum* **77**, 513 (2005).

[5] A. Misiuk, B. Surma, A. Wnuk, C.A. Londos, A. Bukowski, *Cryst. Res. Techn.* **40**, 1812 (2005).

[6] A. Misiuk, B. Surma, J. Hartwig, *Mater. Sci. Eng. B* **36**, 30 (1996).

[7] M. Moreno, B. Jenichen, V. Kaganer, W. Braun, A. Trampert, L. Daweritz, K.H. Ploog, *Phys. Rev. B* **67**, 235206 (2003).

[8] U. Pietch, V. Holý, T. Baumbach, *High Resolution X-Ray Scattering from Thin Films and Multilayers*, Springer-Verlag, Berlin 2004, p. 170.