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# Oxygen precipitation and creation of defects in neutron irradiated Cz-Si annealed under high pressure

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Oxygen precipitation and creation of defects in Czochralski grown silicon (Cz-Si, with interstitial oxygen concentration $1.1 \times 10^{18}$ cm$^{-3}$) subjected to irradiation with neutrons (5 MeV, dose $1 \times 10^{17}$ cm$^{-2}$) and treated under atmospheric and high hydrostatic pressures (HP, up to 1.1 GPa) at 1270 / 1400 K are investigated by spectroscopic and X-Ray (synchrotron) methods. The presence of point defects created by neutron irradiation stimulates oxygen precipitation and creation of dislocations under HP, especially at 1270 K. The effect of pressure treatment is related to changes of concentration and mobility of silicon interstitials and vacancies as well as of the VO – type defects.



**1 Introduction** Oxygen precipitation and creation of extended defects such as dislocations in oxygen containing Czochralski grown silicon (Cz-Si) are markedly affected by the enhancement of hydrostatic pressure (HP) exerted by inert argon ambient during anneals at high temperatures (HT). Oxygen removal from the interstitial positions (oxygen precipitation) is strongly enhanced under HP, especially at about 1270 K [1]. High uniform stress results in the increased effective radius of oxygen interstitial ($O_i$) interaction with nucleation centre for oxygen precipitation and yields a lower pre-exponential factor of the diffusion coefficient of oxygen due to $O_i$ capture by nucleation centres [2].

Similarly, heavy neutron irradiation of Cz-Si has been reported to accelerate the oxygen precipitation at HT, especially at around 1370 K [3]. This effect has been attributed to the defect clusters introduced by neutron irradiation and acting as the cores for oxygen precipitation on heterogeneous nuclei and so shortening the nucleation time [3]. The enhanced oxygen precipitation at about 1170 K has been reported also for Cz-Si irradiated with electrons [4].

The study of the effect of neutron irradiation and of annealing under enhanced pressure (HT - HP treatment) on oxygen precipitation and creation of defects in Cz-Si is reported in this work. As it has been stated earlier, such combined treatment affects properties of Cz-Si in a specific way [5, 6].

**2 Experimental** The 2 mm thick 001 oriented p-type Cz-Si samples of about 12 x 6 mm$^2$ dimension with $O_i$ concentration (determined by Fourier Transform Infrared Spectroscopy, FTIR, measurement accuracy $\pm$ 0.5 x $10^{17}$ cm$^{-3}$), $c_o = 1.1 \times 10^{18}$ cm$^{-3}$, were irradiated with fast neutrons (energy, $E$ = 5 MeV) at

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room temperature to a dose, $D = 1\text{x}10^{17}$ cm$^{-2}$ (these samples will be further denoted as NI). The NI and reference non-irradiated samples (R) were annealed at 1270 K and 1400 K for 5 h under atmospheric ($10^5$ Pa) or 1.1 GPa pressure in Ar atmosphere. The $c_o$ values and sample structure were investigated by FTIR, synchrotron topography (HASYLAB at DESY), photoluminescence (PL, excitation with Ar laser, $\lambda = 488$ nm, at 6 K) and X-ray reciprocal space mapping (XRRSM).

**3 Results and discussion** The effect of HT – HP treatment on the interstitial oxygen concentration in the annealed / HT – HP treated R (reference) and NI samples is presented in Table 1. Annealing for 5 h of the R sample at 1270 K under $10^5$ Pa does not affect $c_o$. This means that oxygen precipitation under atmospheric pressure is negligible, obviously because no nucleation centres for oxygen precipitation are present within the sample volume. No defects were detected for such samples by means of synchrotron topography (Fig. 1A) and X-ray reciprocal space mapping (Fig. 2A). In effect of the similar treatment but under HP the $c_o$ value decreased ($\Delta c_o = 2.5\text{x}10^{17}$ cm$^{-3}$) evidencing the HP – induced oxygen precipitation [7] on the nucleation sites created in Cz-Si owing to initially existing structural disturbances [8]. As it follows from broadened XRRSMs (compare Figs. 2C and 2A), the mentioned oxygen precipitation is concomitant with more disturbed structure of the sample.

Contrary to the case of reference samples, annealing for 5 h of the NI samples at 1270 K under $10^5$ Pa leads to the oxygen precipitation ($\Delta c_o = 1.6\text{x}10^{17}$ cm$^{-3}$). Numerous tiny defects are seen on the topograph (Fig. 1B) while XRRSM for this sample is similar to that of the R sample treated at 1270 K under HP (compare Figs. 2B and 2C).

The treatment of NI at 1270 K under HP leads to the most heavy oxygen precipitation ($\Delta c_o = 5.6\text{x}10^{17}$ cm$^{-3}$, see Table 1). So one can conclude that the presence of irradiation – induced point defects affects the oxygen precipitation in Cz-Si at 1270 K if annealed under HP. The density of oxygen – related defects increased (compare Figs. 1C and 1B) while the mentioned treatment exerted practically no effect on XRRSM (Fig. 2D).

**Table 1** Interstitial oxygen content $c_o$ for annealed / treated R and NI samples.

| HT [K] | HP [Pa] | $c_o$ for sample R [$10^{17}$ cm$^{-3}$] | $c_o$ for sample NI [$10^{17}$ cm$^{-3}$] |
|---|---|---|---|
| 1270 | $1\text{x}10^5$ | 11.1 | 9.4 |
| 1270 | $1.1\text{x}10^9$ | 8.6 | 5.4 |
| 1400 | $1\text{x}10^5$ | 10.4 | 10.6 |
| 1400 | $1.1\text{x}10^9$ | 8.5 | 10.4 |

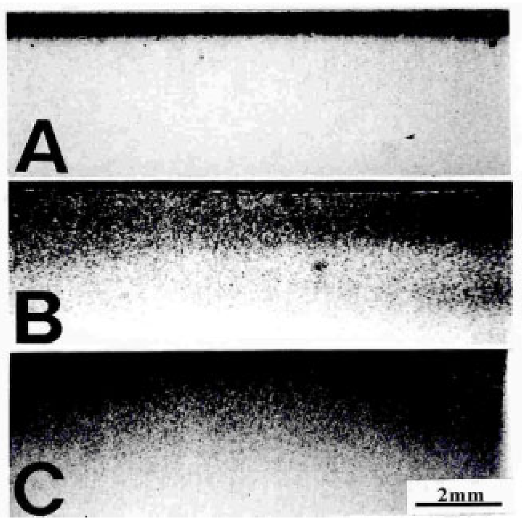


**Fig. 1** Bragg case synchrotron white beam topographs of R (A) and NI samples (B and C) annealed / treated at 1270 K under $10^5$ Pa (A and B) and 1.1 GPa (C).

While the FTIR spectrum of the R sample annealed at 1270 K under 1.1 GPa indicated only absorption at 1107 $cm^{-1}$ evidencing the presence of $O_i$ (Fig. 3A), the treatment of this sample under 1.1 GPa resulted in a weak absorption peaking at about 1213 $cm^{-1}$ (Fig. 3B). This last absorption feature corresponds to the presence of silicon oxide precipitates [9]. Absorption around 1213 $cm^{-1}$ was the highest for the case of NI sample subjected to the treatment under HP (Fig. 3C). The PL spectrum for that last sample indicates the D1 dislocation – related peak at 0.81 eV, almost not detectable for the similarly treated reference R sample (Fig. 4).

Annealing of the R sample at higher temperature, 1400 K under $10^5$ Pa almost does not affect the $c_o$ value (Table 1). Similarly as in the case of annealing at 1270 K, oxygen precipitation does not occur because of the absence of nucleation centres for oxygen precipitation. Almost no extended defects were detected for the annealed R samples by synchrotron topography (Fig. 5A) and X-ray reciprocal space mapping (Fig. 6A).

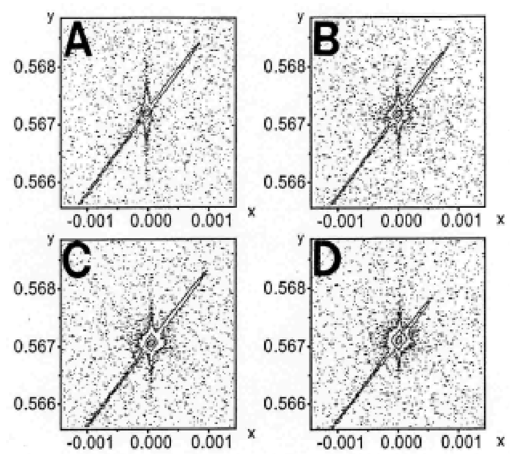


**Fig. 2** XRRSMs of R (A and C) and NI (B and D) samples processed at 1270 K under $10^5$ Pa (A and B) and 1.1 GPa (C and D). The axes are marked in $\lambda/2d$ units ($\lambda$ - wavelength, $d$ - inter-planar distance).

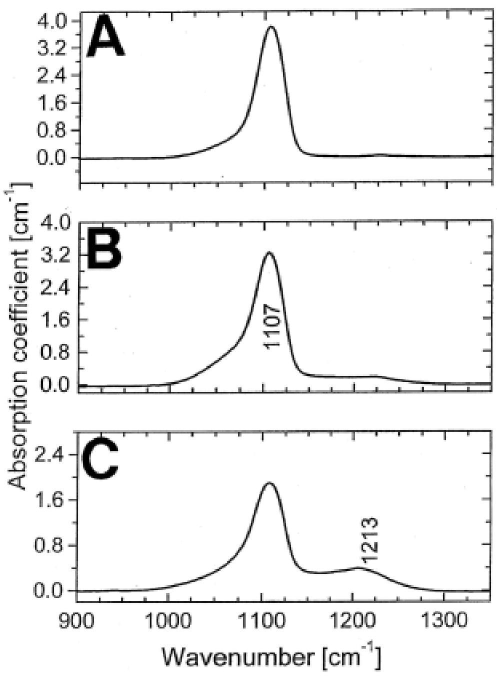


**Fig. 3** FTIR absorption spectra taken at 300 K for R (A) and NI (B and C) samples, annealed / treated at 1270 K under $10^5$ Pa (A and B) and 1.1 GPa (C).

In effect of the similar treatment but under HP the $c_o$ value decreased ($\Delta c_o = 2.6 \times 10^{17}$ $cm^{-3}$, Table 1) evidencing HP – induced oxygen precipitation on the nucleation sites created under HP on as grown structural disturbances [8]. The treatment of the R sample under 1.1 GPa exerted, however, almost no effect on XRRSM (Figs. 6A and B).

Contrary to the case of reference samples R, the annealing / treatment of the NI samples at 1400 K under both $10^5$ Pa and 1.1 GPa leads to negligible oxygen precipitation (Table 1). Well resolved defects with large strain were observed in the synchrotron topographs (Fig. 5B) while XRRSMs for these samples were the same as that of the R samples processed at 1400 K (compare Figs. 6C with 6A and B).

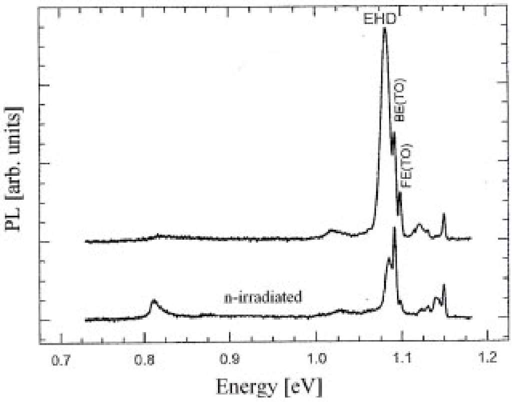


**Fig. 4** PL spectra of reference (non-marked) and neutron – irradiated samples treated at 1270 K under 1.1 GPa. EHD (electron – hole droplet) means the recombination related to electron – hole droplet; BE(TO) and FE(TO) – the transverse optical phonon replicas of bound exciton and of free exciton recombination, respectively.

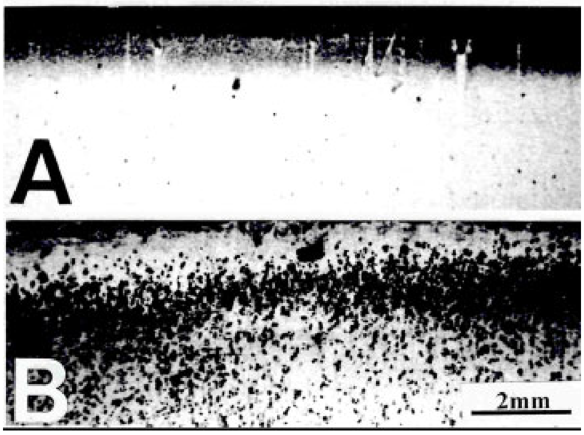


**Fig. 5** Bragg-case white beam topographs of R (A) and NI (B) samples annealed / treated at 1400 K under $10^5$ Pa (A) and 1.1 GPa (C).

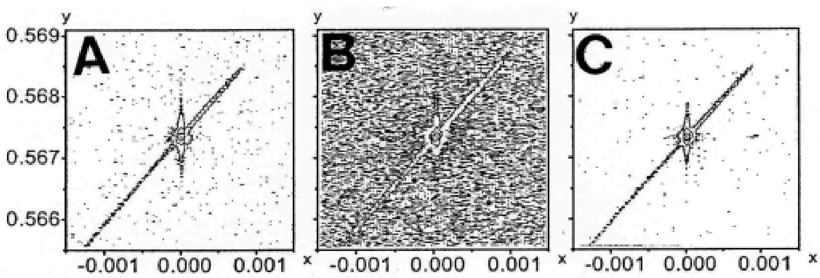


**Fig. 6** XRRSMs of R (A and B) and NI (C) samples annealed / treated at 1400 K under $10^5$ Pa (A) and 1.1 GPa (B and C).

No dislocation – related PL peaks were detected for the processed reference and neutron irradiated Cz-Si samples (Fig. 7). The higher intensity of the EHD line for the processed R samples in comparison to that of the neutron irradiated one evidences the slightly "worsened" crystallographic perfection in the case of NI sample treated at 1400 K – HP (Fig. 7).

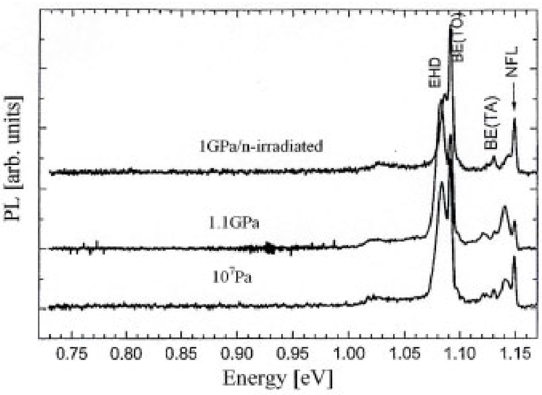


**Fig. 7** PL spectra of reference R and neutron – irradiated NI samples annealed / treated at 1400 K under $10^5$ Pa and 1.1 GPa. BE(TA) means the recombination of transverse acoustic phonon replica of boron bound exciton and NFL - the non – fonon recombination of excitons.

From the above presented results it follows that:

- the effect of neutron irradiation (for applied *E* and *D*) and of the HT – HP treatment on Cz-Si is additive to some extent, at least at HT = 1270 K and HP = 1.1 GPa. Cz-Si represents the non-equilibrium system (the over-saturated Si – O solid solution). Neutron irradiation and the HT – HP treatment done in sequence induce additional nucleation sites for oxygen precipitation [1, 4] and so stimulate oxygen precipitation (Table 1) and the creation of oxygen-containing clusters / precipitates (Figs. 1-3) and of dislocations at the precipitate / matrix boundary (Fig. 4). Also silicon vacancies (V) created at irradiation as well as their complexes with oxygen (VO, $V_xO_y$ [6]) contribute to the mentioned effects;
- at 1400 K – (HT) the over-saturation with oxygen is less pronounced while the mobility of V and of Si interstitials increases. This results in a decreased concentration of nucleation centres, moreover that most of them composed of small oxygen / point defect clusters, dissolve in Si matrix. Only the largest of these nucleation sites survive and grow (Fig. 5), on expense of the smallest ones (Ostwald ripening) and also owing to the enhanced (at 1400 K) mobility of $O_i$'s. The net result would be lowered (in comparison to the effects observed at 1270 K) oxygen precipitation (Table 1), survival and growth of the largest oxygen – related defects (Figs. 5, 6) and lowered concentration of extended defects (compare Figs. 7 and 4).

To conclude, it has been stated that the structure of neutron irradiated and annealed Cz-Si is strongly dependent on the pressure of ambient. Qualitative explanation of the effects observed has been proposed. More adequate explanation of the effects reported demands further investigation of the effect of neutron irradiation and of HT – HP processing on evolution of irradiation – induced defects at the wide range of temperature and hydrostatic pressure.

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