Influence Of Neutron Irradiation On Stress - Induced Oxygen Precipitation In Cz-Si

Jadwiga Bak-Misiuk\textsuperscript{1,a}, Andrzej Misiuk\textsuperscript{2,b}, Barbara Surma\textsuperscript{3,c}, Artem Shalimov\textsuperscript{1,a}, Charalamos A. Londos\textsuperscript{4,d}

\textsuperscript{1}Institute of Physics, PAS, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
\textsuperscript{2}Institute of Electron Technology, Al. Lotnikow 46, 02-668 Warsaw, Poland
\textsuperscript{3}Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland
\textsuperscript{4}University of Athens, Physics Department, Solid State Section, Panepistimiopolis, Zografos, Athens 157 84, Greece

\textsuperscript{a}bakmi@ifpan.edu.pl, \textsuperscript{b}misiuk@ite.waw.pl, \textsuperscript{c}Barbara.Surma@itme.edu.pl, \textsuperscript{d}hlontos@cc.uoa.gr

Keywords: Cz-Si, Neutron Irradiation, Oxygen Precipitation, Annealing, Hydrostatic Pressure, Oxygen Precipitation, Stress.

Abstract

Oxygen precipitation and creation of defects in Czochralski grown silicon with interstitial oxygen concentration \(9.4 \times 10^{17} \text{ cm}^{-3}\), subjected to irradiation with neutrons (5 MeV, dose \(1 \times 10^{17} \text{ cm}^{-2}\)) and subsequently treated for 5 h under atmospheric and high hydrostatic pressures (\(HP\), up to 1.1 GPa) at 1270 / 1400 K, were investigated by spectroscopic and X - Ray methods. Point defects created by neutron irradiation stimulate oxygen precipitation and creation of dislocations under \(HP\), especially at 1270 K. The effect of pressure treatment is related to changed concentration and mobility of silicon interstitials and vacancies as well as of the V\(_n\)O\(_m\) – type defects.

Introduction

Oxygen is a common residual impurity in silicon grown by Czochralski method (Cz-Si). Most oxygen atoms in the silicon lattice occupy interstitial positions (O\(_i\)). During annealing at high temperature (\(HT\)), oxygen atoms agglomerate in the form of precipitates of different sizes [1]. Oxygen precipitation in Cz-Si and resulting creation of extended defects, such as dislocations, are markedly affected by enhanced hydrostatic pressure (\(HP\)) exerted by inert gas ambient during annealing [2]. Removal of oxygen from interstitial positions (oxygen precipitation) is strongly enhanced under \(HP\), especially at about 1170 - 1270 K [3]. High stress exerted by \(HP\) of ambient gas results in the increased effective radius of the oxygen interstitial interaction with the nucleation center for oxygen precipitation and yields a lower pre - exponential factor of the diffusion coefficient of oxygen diffusion in silicon due to O\(_i\) capture by the nucleation centers activated during the \(HT - HP\) treatment [4].

Neutron irradiation of Cz-Si produces point defects also affecting oxygen precipitation [5]. Oxygen and silicon interstitials (O\(_i\) and Si\(_i\)), vacancies (V) and their complexes are the main defects in neutron – irradiated silicon. \(HP\) affects oxygen precipitation in neutron - irradiated Cz-Si mostly through its effect on the transformation of VO and V\(_m\)O\(_n\) complexes; the last ones can act as the nuclei for oxygen precipitation [5, 6]. Enhanced formation of plate - like oxygen precipitates was found in neutron - irradiated Cz-Si samples treated at 1270 K under 1.1 GPa [7]. First results on the effect of uniform stress on oxygen precipitation at \(\geq 1270\) K in (001) oriented Cz-Si with interstitial...
oxygen concentration \( c_o = 1.1 \times 10^{18} \text{ cm}^{-3} \) and with point defects introduced by neutron irradiation have been reported recently [8].

More detailed study of the effect of neutron irradiation and of annealing under enhanced pressure on oxygen precipitation and the creation of defects in (111) oriented Cz-Si with lower oxygen content \( (c_o = 9.5 \times 10^{17} \text{ cm}^{-3}) \) is now presented.

**Experimental**

The (111) oriented Cz-Si samples with initial interstitial oxygen concentration, \( c_o = 9.5 \times 10^{17} \text{ cm}^{-3} \) were irradiated with fast neutrons, with energy, \( E = 5 \text{ MeV} \), to a dose \( D = 1 \times 10^{17} \text{ cm}^{-2} \). Next the non-irradiated reference samples (R) and the neutron-irradiated ones (NI) were treated for 5 h at 1270 K and 1400 K under hydrostatic argon pressure \( 10^5 \text{ Pa} \) and 1.1 GPa. Oxygen precipitation and sample structure were investigated by Fourier Transform Infrared Spectroscopy (FTIR, done at 300 K), high-resolution X-Ray diffractometry (to record reciprocal space maps, XRRSMs) and by photoluminescence (PL) measurements. PL from investigated samples was excited at 6 K with Ar laser, \( \lambda = 488 \text{ nm} \).

**Results and Discussion**

The effect of \( HT - HP \) treatment on \( O_i \) concentration in the annealed / \( HT - HP \) treated R (reference) and NI samples is presented in Table 1. The concentration of \( O_i \) decreases in effect of the treatment; this decrease is most pronounced in the case of neutron-irradiated samples. The concentration of vacancies tends to decrease at annealing, especially if done under \( HP \). Most probably, the \( V_nO_m \) and similar defects produced by neutron irradiation and transformed at processing at higher temperature (processing temperature was reached after 10 min. starting from about 300 K) act as the nucleation centres for subsequent oxygen precipitation at 1270 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure</th>
<th>( c_o ) [cm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>( 10^5 \text{ Pa} )</td>
<td>( 9.4 \times 10^{17} )</td>
</tr>
<tr>
<td>R</td>
<td>1.1 GPa</td>
<td>( 8.7 \times 10^{17} )</td>
</tr>
<tr>
<td>NI</td>
<td>( 10^5 \text{ Pa} )</td>
<td>( 7.7 \times 10^{17} )</td>
</tr>
<tr>
<td>NI</td>
<td>1.1 GPa</td>
<td>( 6.5 \times 10^{17} )</td>
</tr>
</tbody>
</table>

XRRSMs of annealed / treated R and NI samples are presented in Fig. 1. X-Ray diffuse scattering from the R samples annealed under \( 10^5 \text{ Pa} \) origins from uniformly distributed small agglomerates of point-like defects (Fig. 1A). Plate-like oxygen precipitates and related dislocations loops are created in the R samples treated under \( HP \) while the distribution of scattered X-Rays is markedly changed (Fig. 1C). The effect of \( HP \) during processing is distinctly different for the NI samples in comparison to that for the R ones (Fig. 1B, D). The X-Ray diffuse scattering intensity from the NI sample, neutron-irradiated and next treated at 1270 K under \( HP \), decreased in comparison to that for the NI sample annealed under \( 10^5 \text{ Pa} \) (Fig. 1B, D). An analysis [9] of the diffuse scattering intensity for the neutron-irradiated samples indicates on a creation of small dislocation loops; their dimensions increase in effect of the \( HT - HP \) treatment.

Decrease of the diffuse scattering intensity is accompanied with the decreased concentration of vacancies. This fact provides an evidence that dislocation loops are of the vacancy type. It means that the presence of point defects (vacancies) created by neutron irradiation stimulates the generation of dislocation loops. The effect of pressure treatment seems to be related to the \( HP \)-affected concentration and mobility of \( \text{Si}_i, O_i \), and of \( V \) as well as of their complexes (compare [6, 10]). It is visible that the structure of neutron-irradiated Cz-Si samples is dependent on stress exerted by hydrostatic pressure applied during processing.
Fig. 1. Reciprocal space maps of Cz-Si (A and C: non-irradiated R samples; B and D - neutron-irradiated NI samples) treated for 5 h at 1270 K under $10^5$ Pa (A and B) and 1.1 GPa (C and D). Coordinates are given in $\lambda/2d$ units; $\lambda$ - wavelength and $d$ - interplanar distance.

Absorption spectra of the processed R and NI samples are shown in Figs 2 and 3. After annealing / treatment of the samples, the absorption band at 1107 cm$^{-1}$ (originating from the presence of O$_2^+$'s) dominates the spectra. The absorption band at 1107 cm$^{-1}$ is related to the stretching vibration mode of the Si - O bond; this absorption line is commonly used for determination of the interstitial oxygen concentration in silicon [1]. The weak absorption peak at about 1225 cm$^{-1}$ is related to the presence of oxygen precipitates. Weak absorption around 1213 cm$^{-1}$ also corresponds to the presence of silicon oxide precipitates [11]; it is observed usually in the case of annealed Cz-Si samples with comparatively high oxygen concentration. The FTIR spectra of the R and NI samples processed at 1270 K under $10^5$ Pa and 1.1 GPa are very similar and differ mainly in respect of the intensities of absorption peaks (Figs 2, 3).

Fig. 2. FTIR absorption spectra for R (1, solid line) and NI (2, dots) samples, annealed for 5 h at 1270 K under $10^5$ Pa.
Absorption was higher in the R samples than that in the NI ones. Still small differences in the shape of absorption bands for the R and NI samples suggest that decrease of $c_c$ (Table 1) is related to creation of small oxygen-containing clusters, which, however, can not be clearly detected in the absorption spectra. In the HT-HP treated R samples, the absorption band at about 1070 cm$^{-1}$, related to the presence of oxygen precipitates, is more distinct than in the NI samples (Fig. 3).

PL spectra of the R and NI samples processed at 1270 K are presented in Figs 4 and 5. The PL spectrum of R sample processed under 1.1 GPa evidences the presence of dislocations as confirmed by the broad dislocation-related D1 peak at about 0.81 eV. Broadening of this peak is probably caused by non-uniform strain related to the presence of oxygen-containing defects formed in Si in effect of pressure-induced oxygen precipitation. The PL peak at 1.07 eV observed for the processed R and NI samples is related to some non-identified defects, possibly also associated with dislocations created in effect of the treatment.
As seen in the PL spectrum of the NI sample treated under 1.1 GPa, its defect structure is treatment - specific while low intensity of PL near 1.1 eV evidences the presence of non - radiative recombination centres in a high concentration. The PL spectrum of the HT - HP treated NI sample also indicates the D1 dislocation – related peak at 0.81 eV (Fig. 5). The PL peak at about 0.92 eV originates from vacancy clusters. These peaks were not detected for the similarly treated reference R sample as well as for the NI samples annealed under atmospheric pressure (Figs 4, 5).

Similarly as in the case of non - irradiated, reference R samples, processing of the NI samples at 1400 K under 10^5 Pa and 1.1 GPa leads to less pronounced oxygen precipitation (compare [8]). The (111) XRRSMs patterns for the R and NI samples processed at 1400 K under 1.1 GPa are presented in Fig. 6. The treatment under HP results in an enhanced intensity of diffusively scattered X - Rays (compare Figs 6A,B with 6C).

In the case of HT - HP treated NI samples the X-ray diffuse scattering is distinctly enhanced (see also Fig. 1A and B) evidencing the presence of dislocation loops in a low concentration. However, even in this case the defect concentration was higher than that for the similarly treated non - irradiated R samples; for the last ones an influence of applied pressure at annealing on the defect structure was almost negligible.

From above presented results it follows that the effects of neutron irradiation and of the HT – HP treatment on Cz-Si are to some extent additive.

Fig. 5. PL spectra of NI samples treated at 1270 K under 10^5 Pa and 1.1 GPa. For meaning of EHD, BE(TO) and FE(TO) – see caption of Fig. 4.

Fig. 6. Reciprocal space maps of NI (A) and R samples (B, C) processed for 5 h at 1400 K under 1.1 GPa (A and B) and under 10^5 Pa (C). Coordinates are given in λ/2d units where λ - wavelength and d - interplanar distance.
At room temperature Cz-Si can be considered as the non-equilibrium system (the over-saturated Si – O solid solution). Silicon vacancies as well as their complexes with oxygen (such as VO and \( V_nO_m \)) contribute to oxygen precipitation at HT.

Sequentially performed neutron irradiation and the HT – HP treatment introduce additional nucleation sites for oxygen precipitation [8], especially at lower temperatures (before reaching the treatment temperature) when the reaction channel \( VO \rightarrow VO_2 \rightarrow VO_3 \) has been reported to be affected by HP [12].

Enhanced hydrostatic pressure at annealing results in more numerous nucleation centres and so stimulates oxygen precipitation and creation of different oxygen-containing clusters / precipitates as well as, in the case of sufficiently large oxygen precipitations, also of dislocations at the precipitate / matrix boundary. This last effect results from the changed misfit at the mentioned boundary, surpassing the critical one for creation of extended defects [2].

**Conclusions**

It has been stated that the structure of neutron irradiated and annealed Cz-Si is strongly dependent on the pressure of ambient. The effect of enhanced hydrostatic pressure during annealing is distinctly different for the neutron-irradiated Cz-Si samples in comparison to the case of non-irradiated Cz-Si.

Presented results confirm that the pressure treatment promotes oxygen precipitation process in neutron-irradiated Cz-Si. In the conditions of enhanced pressure a lot of additional defects, being the embryos of nucleation centers for oxygen precipitation, are generated. In consequence, interstitial oxygen atoms are removed from the Si lattice to form different oxygen-related clusters and precipitates as well as other extended defects, such as dislocations.

**Acknowledgements**

The authors express their gratitude for Mr M. Prujszczyk from the Institute of Electron Technology, Warsaw, Poland for performing the high temperature - pressure treatments of investigated samples.

**References**