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Dependence of photoluminescence of silicon on conditions of pressure-annealing

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Abstract

Effect of annealing at (720-1000) K/1400 K under argon pressure up to 1.2×10^{9} Pa on photoluminescence related to defects created in oxygen-containing (Czochralski grown or oxygen-implanted) silicon was investigated by optical, synchrotron, X-ray and related methods. For the samples pressure-treated at 1400 K the intensity of dislocation-related photoluminescence lines was found to be reduced in comparison to that for the samples annealed at ambient pressure. An increase of photoluminescence intensity at 0.97–1.04 eV, a reduction of X-ray diffuse scattering intensity as well as creation of large (up to 15 μm) oxygen-related defects were stated for the samples annealed at 1400 K under high pressure. An explanation of observed phenomena is proposed.

Keywords: Silicon; Implantation; Stress; Photoluminescence; Defects

1. Introduction

It is well known that various defects [e.g. oxygen clusters (OC), oxygen precipitates (OP) or even continuous SiO_2 layers] are generated in effect of high temperature anneals in oxygen containing Czochralski-grown silicon (Cz–Si) and in oxygen-implanted silicon [1].

Such defects, especially OP and buried oxide (BOX) layers, exert stress on surrounding Si matrix because of much higher volume of oxygen precipitates of SiO_{2-x} composition in comparison to that of silicon. To release this stress, silicon interstitials, Si_i, are emitted and so the 'secondary' defects (such as dislocations) are created at the OP (BOX)/Si matrix boundary. The phenomenon of creation of oxygen-related defects in Si is still extensively studied, also because of importance of oxygen-rich Si and SOI (silicon on oxide) structures in modern microelectronics.

Enhanced hydrostatic pressure (HP) of gas (argon) ambient during sample annealing (denoted below as HP–HT treatment) can cause diminishing of the 'higher SiO_2 volume effect'. The shear stress at the Si/oxygen defect boundary can be lower at HP because of much larger compressibility of SiO_2 in comparison to that of Si [2]. Such treatment results in specific stress-related phenomena, e.g. in pressure-stimulated oxygen precipitation [3] with creation of different oxygen-related defects [4].

The (defects-related) photoluminescence (PL) of Cz–Si with interstitial oxygen concentration, c_o, up to 1.1×10^{18} cm^{-3} and of oxygen-implanted silicon with maximum oxygen concentration up to above 10^{20} cm^{-3} was investigated in this work after sample treatment at different pressure–temperature conditions.

2. Experimental

Single crystalline (001) oriented bulk Cz–Si wafers with initial c_o up to above 10^{18} cm^{-3} and (111) oriented floating-zone grown silicon (FZ–Si) samples, implanted by O^+ with energy of 200 keV and doses, d, up to 10^{17} cm^{-2}, were investigated.

The samples were subjected to sequential anneals at pressure up to 1.2 GPa. The first one- or two-step pre-anneal at (720–1000) K, typically under atmospheric pressure of nitrogen for up to 96 h, was performed to

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remove the post-implantation defects in oxygen-implanted FZ–Si and to create nucleation centres for oxygen precipitation (NCs) in Cz–Si. The second anneal at atmospheric or enhanced pressure of argon (HP–HT treatment) was performed typically at 1400 K, for up to 10 h, to promote massive oxygen precipitation on before-created NCs. Pressure exerted by argon atmosphere was hydrostatic at the applied treatment conditions.

After each processing step it were measured: (a) PL at 14 K, using an argon laser with λ=488 nm as the excitation source, (b) the oxygen interstitials concentration [by Fourier transform infrared spectroscopy (FTIR) using conversion factor equal to 2.45], (c) the lattice parameter of silicon, a (at 295 K) with an accuracy $\pm$0.000005 nm (by the Bond method), and (d) diffuse scattering of X-rays (by reciprocal space mapping). X-ray measurements were performed on Philips MRD diffractometer equipped with conventional X-ray tube operating at 1.4 kW with CuKα_1 radiation. A high resolution experimental set-up was realised by employing a four-crystal Ge (220) Bartels-type monochromator in the primary beam and a channel-cut double-reflection Ge (220) analyser in the diffracted beam. Some samples were investigated by synchrotron topography at ESRF Grenoble, transmission electron microscopy and optical microscopy after selective chemical etching.

3. Results

PL of (pressure) annealed oxygen-containing silicon samples was dependent on initial oxygen concentration, on the sample defect structure and on the HP–HT treatment conditions.

Annealing of Cz–Si samples with NCs at (1220–1400) K/10^5 Pa caused pronounced oxygen precipitation with creation of different oxygen-related defects. It resulted in dislocation-related PL. The same was stated for the samples after the HP–HT treatment at (1070–1170) K. For example, the D1 and D2 dislocation-related PL lines were observed in the bulk Cz–Si samples (initial c_o=8.2×10^{17} cm^{-3}), subjected to 'nucleation' pre-annealing at 10^5 Pa and afterwards HP–HT treated at 1070, 1120 or 1170 K under 3×10^8 Pa. Intensity of the D1 line at 0.81 eV decreased and that of the D2 line at 0.87 eV increased with treatment temperature.

The same sample annealed at 1220 K at atmospheric pressure indicated presence of the PL lines at 0.81, 0.84 and 0.87 eV (Fig. 1a), whereas only weak PL line at about 0.92 eV was observed after the treatment at 1220 K/1.2×10^9 Pa/5 h. The dislocation-related PL lines disappeared almost completely after the HP–HT treatment at 1400 K (Fig. 1b).

Defect images in the Cz–Si samples pressure treated at 1400 K were resolved by synchrotron topography only in the case of comparatively low initial c_o values (Fig. 2). Defects-related strain fields in the HP–HT treated Cz–Si samples with c_o>7.5×10^{17} cm^{-3} were overlapping.

As it follows from TEM observation, the density of extended defects (mostly of stacking faults, SF, and of OP) was much lower (for one or more orders of magnitude) after the treatment at 1400 K/10^9 Pa/5 h for the samples pre-annealed at (720–1000) K/10^5 Pa for 20 h and afterwards pressure-treated at 1400 K for 5 h, in comparison to that for the samples treated at 1400 K/(10^5–10^7) Pa. Simultaneously the defect dimensions increased up to above 15 μm.

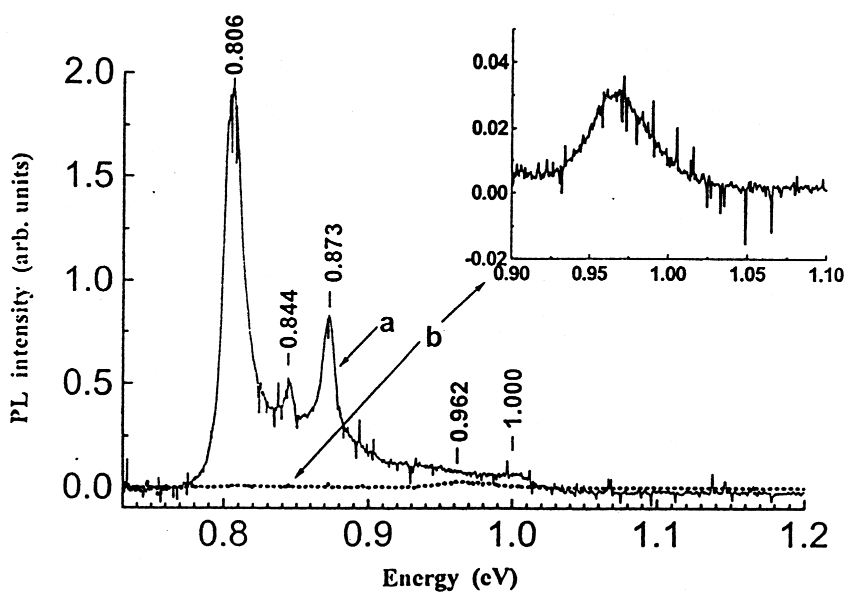

Fig. 1. Effect of annealing conditions on PL of Cz–Si samples (initial c_o=8.2×10^{17} cm^{-3}). (a) Sample pre-annealed at 10^5 Pa: 720 K/20 h+920 K/20 h and afterwards annealed at 1220 K/10^5 Pa for 20 h (c_o diminished to 2.2×10^{17} cm^{-3}). (b, insert) Sample pre-annealed at 10^5 Pa: 870 K/20 h+1000 K/20 h and pressure-treated at 1400 K/1.2×10^9 Pa for 5 h (c_o=3.2×10^{17} cm^{-3}).

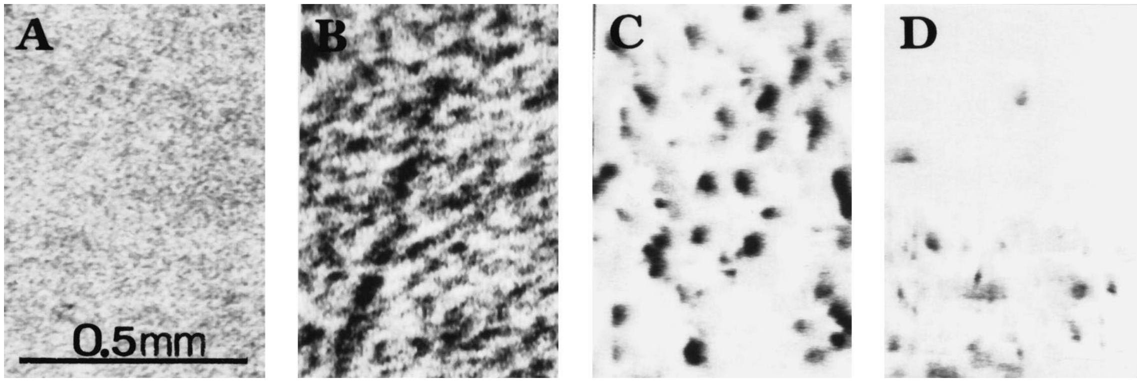

Fig. 2. White beam transmission synchrotron topographs ($\lambda \approx 0.04$ nm, 111 reflection) of (001) oriented Cz–Si samples with initial $c_o = 6.5 \times 10^{17}$ cm^{-3}, pre-annealed at 720 K/10^5 Pa for 96 h and afterwards HP–HT treated: (A) at 1400 K/10^7 Pa/0.5 h ($c_o = 6.35 \times 10^{17}$ cm^{-3}); (B) at 1400 K/1.15×10^9 Pa/0.5 h ($c_o = 5.6 \times 10^{17}$ cm^{-3}); (C) at 1400 K/10^7 Pa/5 h ($c_o = 5.2\text{x}10^{17}$ cm^{-3}); (D) at 1400 K/10^9 Pa/5 h ($c_o = 5.3 \times 10^{17}$ cm^{-3}).

Optical observations of etch pits after selective chemical etching in the Yang solution confirmed diminishing of the density of saucer pits on the sample surface for the samples with $c_o = 6.5 \times 10^{17}$ cm^{-3} treated at 1400 K/HP.

Contrary to that observation, the density of near-surface stacking faults increased considerably with HP after the treatment at HP/1400 K for (0.5–5) h.

Reciprocal lattice maps of the Cz–Si samples subjected to similar HP–HT treatments are presented in Fig. 3.

PL spectra for some HP–HT treated oxygen-implanted samples (FZ–Si, oxygen dose $d = 10^{16}$ cm^{-2}) are shown in Figs. 4 and 5.

Reciprocal lattice maps and FTIR data of the same samples are presented in Figs. 6 and 7. Lower intensity of X-ray diffuse scattering (Fig. 6) and decreased intensity of infrared absorption peaks at 830, 1080 and 1280 cm^{-1} (Fig. 7) were observed typically in the samples treated at high HP.

The lattice parameter $a_{295\ \mathrm{K}}$ of the oxygen-implanted silicon samples was found to be dependent on treatment conditions. For the as-implanted FZ–Si sample ($d = 10^{16}$ cm^{-2}) it was equal to 0.543063 nm. The lattice parameter was of the highest value (0.543076 nm) for such sample subjected to the one-step treatment at 720 K/1.2×10^9 Pa or at 1400 K/10^5 Pa for 10 h and of the lowest one (0.543058 nm) for the same sample after the two-step treatment at 720 K + at 1400 K.

4. Discussion

The effect of enhanced hydrostatic pressure on defects-related photoluminescence of silicon samples annealed at 1400 K was investigated in this work. According to our knowledge, it is the first report on the title problem.

It is generally accepted that creation of defects in annealed silicon is critically dependent on presence of interstitial oxygen and related to its precipitation from the over-saturated Si–O solid solution [2–4]. We investigated Czochralski grown, Cz–Si, silicon samples containing uniformly distributed oxygen admixture with c_o from 6.5×10^{17} to 1.1×10^{18} cm^{-3} (maximum interstitial oxygen concentration attainable for bulk Si) and the oxygen implanted FZ–Si samples (typical oxygen doses 10^{14}–10^{16} cm^{-2}) with local maximum c_o (near oxygen ion range, R_p, in our case close to 0.4 μm, $\Delta R_p = 0.09$ μm) in the

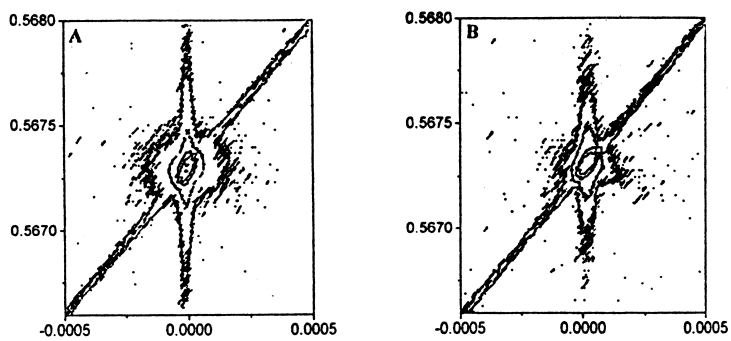

Fig. 3. Two-dimensional reciprocal space Bragg maps recorded near 004 reciprocal lattice point for (001) oriented Cz–Si samples with initial $c_o = 1 \times 10^{18}$ cm^{-3}, pre-annealed at 720 K for 20 h ($c_o = 9.1 \times 10^{17}$ cm^{-3}) and afterwards HP–HT treated at: (A) 1400 K/10^7 Pa for 5 h ($c_o = 8.5 \times 10^{17}$ cm^{-3}), and (B) 1400 K/10^9 Pa for 5 h ($c_o = 7.6 \times 10^{17}$ cm^{-3}). CuKα_1 radiation. Axes are marked in $\lambda/2d$ units (λ, wavelength; d, distance between the crystallographic planes).

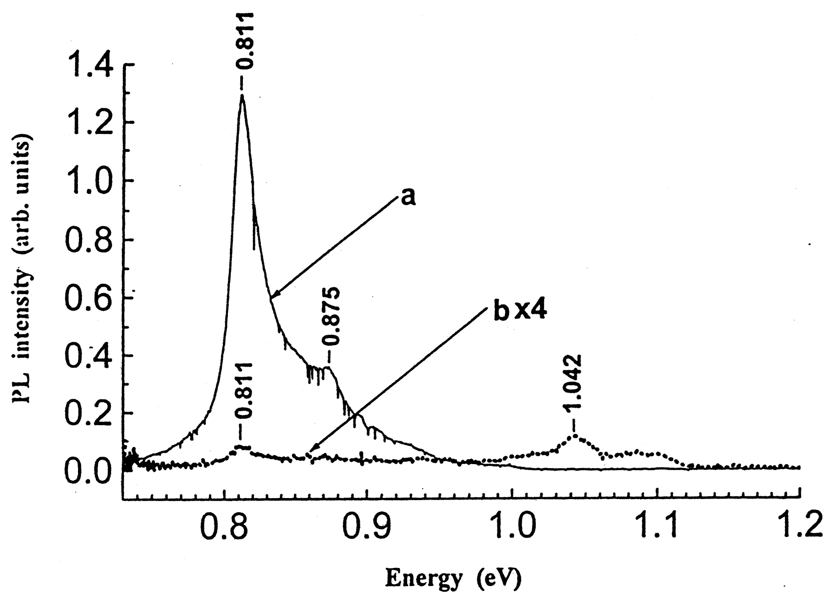

Fig. 4. Effect of pressure on PL of oxygen-implanted FZ–Si sample ($d=10^{16}$ cm^{-2}, maximum $c_o \approx 3\times10^{20}$ cm^{-3}) treated for 5 h: sample (a) at 1400 K/10^5 Pa, and sample (b) at 1400 K/6×10^8 Pa.

(4×10^{18}–4×10^{20}) cm^{-3} range. It means that relative oxygen concentration (in respect to the total number of atoms in the sample, within the oxygen-containing part of the sample) reached ≈0.01% (for Cz–Si samples) and ≈1% (for oxygen-implanted samples).

Annealing of the bulk oxygen-rich Cz–Si samples at 10^5 Pa (atmospheric pressure) resulted typically in appearance of strong PL lines at 0.81, 0.87, 0.94 and 1.0 eV (compare Fig. 1a) obviously related to dislocations created during precipitation of oxygen (such PL peaks denominated D1, D2, D3 and D4 have been observed in plastically deformed Si [5]). The much weaker PL peak at 0.84 eV was of the same energy as that reported for recombination between oxygen-containing thermal donors (created at 720/920 K) and the D1 dislocation acceptor [6]. Such thermal donors, however, were not detected in this sample by electrical measurements. Intensity of the dislocation-related PL peaks was dependent on conditions of pre-annealing at ≤1000 K and of the HP–HT treatment.

Enhanced (up to 1.2×10^9 Pa) pressure of argon ambient during sample treatment at 1400 K resulted in almost complete quenching of dislocation-related PL with appearance of the weak PL at (0.97–1.04) eV (e.g. samples b in Figs. 1 and 4). The origin of this PL is not clear at present.

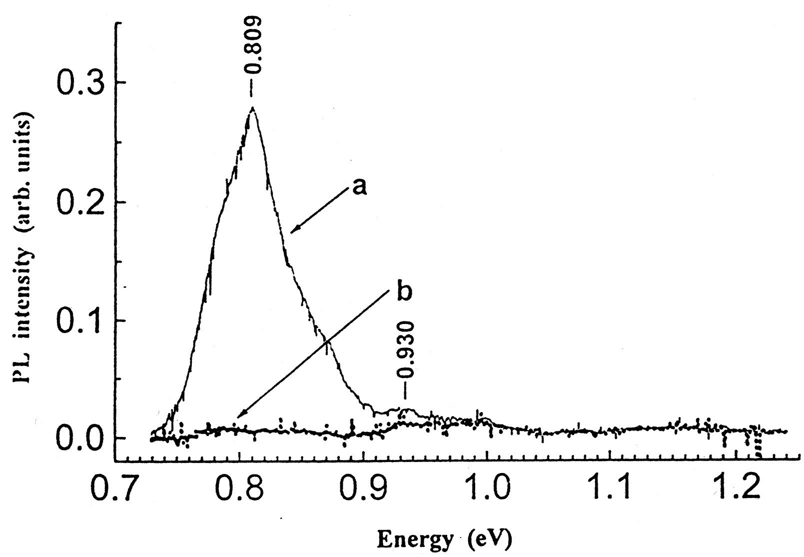

Fig. 5. Effect of HP on PL of oxygen-implanted ($d=10^{16}$ cm^{-2}) FZ–Si sample subjected to HP–HT treatment at: (a) 720 K/1.2×10^9 Pa/10 h+1400 K/10^5 Pa/5 h; (b) 720 K/10^5 Pa/10 h+1400 K/10^9 Pa/5 h.

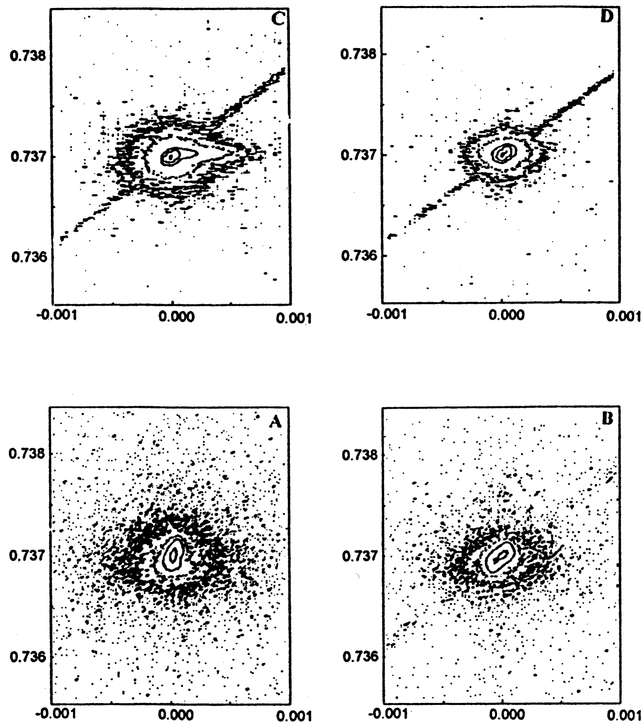

Fig. 6. Two-dimensional reciprocal space Bragg maps recorded near 400 reciprocal lattice point for (111) oriented FZ–Si oxygen-implanted samples ($d=10^{16}$ cm^{-2}), subjected to following treatments: (A) 1400 $K/10^5$ Pa for 10 h; (B) 1400 $K/6\times10^8$ Pa for 10 h; (C) 720 $K/1.2\times10^9$ Pa/10 h+1400 $K/10^5$ Pa/5 h; (D) 720 $K/10^5$ Pa/10 h+1400 $K/1.2\times10^9$ Pa/5 h. $CuK\alpha_1$ radiation. Axes are marked in $\lambda/2d$ units (λ, wavelength; d, distance between the crystallographic planes).

As it has been detected also by other applied methods, pressure-annealing at 1400 K of Cz–Si samples with initial oxygen interstitials concentration in the $(6.5–1.1)\times10^{18}$ cm^{-3} range resulted in dramatic changes of their defect structure. Large strain fields (Fig. 2), obviously related to comparatively large oxygen precipitates, were created. Existence of large oxygen-related defects was confirmed by TEM observations. Such samples indicate also diminished intensity of X-ray diffuse scattering (Fig. 3). The latter can be interpreted as an indication of lowered dislocation density [7] in the samples HP-treated at 1400 K. Optical observations of etch pits after chemical selective etching in the Yang solution confirmed the HP-induced decrease of the density of defects revealed as shallow etch pits. On the other hand, the concentration of stacking faults in such samples was higher. Simultaneously the oxygen concentration in the form of interstitials, c_o, was lower for the samples HP-treated at 1400 K, in comparison to that annealed for the same time under 10^5 Pa.

In spite of different (local) character of oxygen distribution and of much higher oxygen concentration (up to above 10^{20} cm^{-3}) in the oxygen-implanted silicon samples, the HP–HT treatment at 1400K caused similar effects as that detected for bulk Cz–Si. The dislocation-related photoluminescence, quite strong for the samples annealed at 1400 $K/10^5$ Pa (sample a in Fig. 4), disappeared almost completely in effect of the same treatment but at HP (sample b in Fig. 4). The PL peak at 1.04 eV observed for the last sample resembles that detected in reactively etched silicon, presumably related to some intrinsic point defects [8].

Pre-annealing at (720–870) K (to remove radiation defects from oxygen implantation) exerts some effect on PL spectra, but just the conditions of treatment at 1400 K seem to be decisive in this respect. The sample pre-annealed at 720 $K/1.2\times10^9$ Pa and then annealed at 1400 $K/10^5$ Pa indicated wide dislocation-related PL peaking at

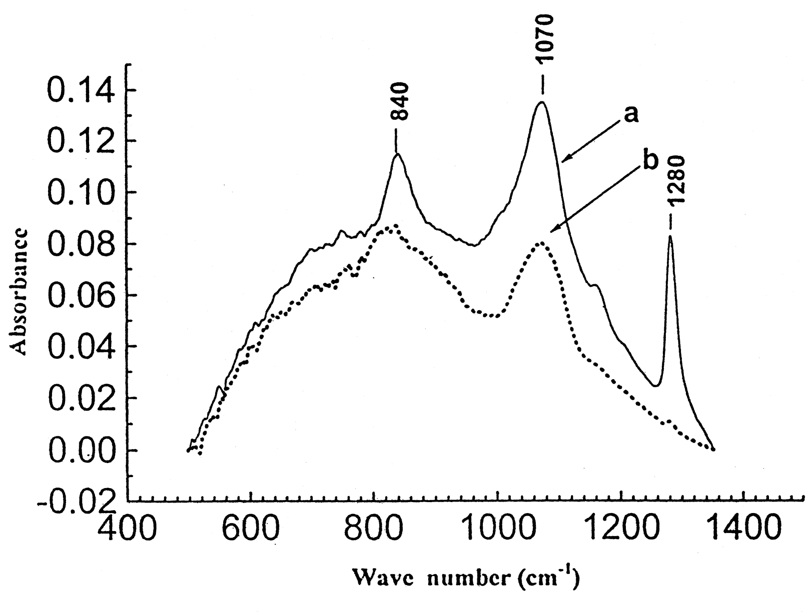

Fig. 7. FTIR data for FZ–Si O^+-implanted samples ($d=10^{16}$ cm^{-2}), subjected to following treatments: (a) 720 $K/1.2\times10^9$ Pa/10 h+1400 $K/10^5$ Pa/5 h; (b) 720 $K/10^5$ Pa/10 h+1400 $K/1.2\times10^9$ Pa/5 h.

0.81 eV, whereas just enhanced pressure during annealing at 1400 K caused almost complete disappearance of PL in the investigated spectral range (compare Figs. 4 and 5). X-ray reciprocal space maps indicated pronounced reduction of X-ray diffuse scattering intensity for the samples treated at 1400 K/1.2×10^9 Pa (Fig. 6), similarly to effect observed for pressure-treated Cz–Si (Fig. 3).

FTIR data for the pressure-treated oxygen-implanted samples (Fig. 7) confirmed that oxygen was contained mostly in precipitates (the 1107 cm^{-1} line from oxygen interstitials, always observable in Cz–Si, was not detected in the HP-treated oxygen-implanted FZ–Si samples). Absorption at about 840 and 1070 cm^{-1} is typical for FTIR spectra of non-stoichiometric silicon dioxide, SiO_{2-x}. The relatively sharp absorption line at 1280 cm^{-1} can be related to structural defects located probably at the SiO_{2-x}/Si interface. Such absorption band has been reported [9] for two-fold co-ordinated (O–Si–O) silicon defect of SiO_2.

The lattice parameter, $a_{295\ K}$, value, determined by the Bond method, corresponds to its mean value for the top, about 4 μm thick surface layer of FZ–Si containing post-implantation defects and most of implanted oxygen atoms. Detailed analysis of the treatment-induced $a_{295\ K}$ changes is impossible at present because of too many parameters influencing its value. One can speculate only that an increase of $a_{295\ K}$ from 0.543063 nm for the as-implanted sample to 0.543076 nm for that after the one-step treatment/anneal at 720 or 1400 K is related to dominating effect of annealing-induced removal of the post-implantation defects with oxygen atoms being placed in the interstitial positions (lattice parameter of silicon increases with c_o). The decrease of $a_{295\ K}$ to 0.543058 nm after two-step processing at 720 K/HP (creation of NCs) and at 1400 K/10^5 Pa (oxygen precipitation on NCs) can be related to next removal of O_i from the interstitial positions with creation of oxygen precipitates and other defects.

The most striking effect of annealing the oxygen-containing silicon samples at enhanced pressure is the almost complete absence of the dislocation-related D1, D2, D3 and D4 PL lines in the oxygen-containing silicon samples subjected to the treatment at 1400 K/HP (Figs. 1, 4, 5). Also diminished X-ray diffuse scattering intensity for the samples treated at 1400 K/HP (Figs. 3 and 6) can be considered as a proof of decreased concentration of dislocations in such samples.

It means that dislocations were not created in oxygen-containing Si at 1400 K/HP, quite opposite to effect stated for the samples annealed at 1400 K under atmospheric pressure. As it follows from synchrotron topographs and TEM, only limited number of oxygen-related defects can be detected in such 'no PL' samples, but some of defects were of much larger dimension than that in the samples annealed at 1400 K/(10^5–10^7) Pa (Fig. 2). From FTIR data it follows that the concentration of oxygen interstitials (remaining to be dissolved in the silicon matrix) was lower in the samples treated at 1400 K/HP, as compared to the case of samples annealed at 1400 K/10^5 Pa. So one can assume that most oxygen atoms in the samples treated at 1400 K/HP are transformed into the form of much smaller defects than that in the samples annealed at 1400 K/10^5 Pa.

So the following question demands explanation: why dislocations were not observed in the samples pressure-annealed at 1400 K. It must be admitted that HP-stimulated creation of dislocations-related defects was reported for the case of oxygen-rich Cz–Si samples pressure-treated at lower temperatures (up to about 1230 K), as it followed e.g. from enhanced X-ray diffuse scattering intensity [10]. Diminishing of defect sizes and defect concentration rise for the oxygen-containing Cz–Si samples treated at ≤1230 K/HP were stated [11].

Most Cz–Si samples investigated in this study were subjected to pre-annealing at (720–1000) K so there were created nucleation centres (NCs) for oxygen precipitation following at >1000 K. Large concentration of defects (created by implantation) existed 'from the very beginning' in the oxygen-implanted samples, creating NCs for oxygen precipitation at 1400 K. During annealing at 1400 K some part of NCs served as the core for growing precipitates, silicon interstitials were emitted and dislocations created, both in effect of growing misfit at the OP/Si matrix boundary as well of 'condensation' of silicon interstitials removed from growing precipitate. On the other hand, some too small NCs were dissolved at 1400 K in the Si matrix supplying oxygen for growth of sufficiently large OPs.

Smaller NCs are stabilised at HP conditions [11] so they are more numerous in the HP-annealed samples. The treatment temperature (1400 K) was, however, high enough to cause partial 'dissolution' of the smallest defects. Both, dissolution of the smallest defects and growth of the larger ones, would be, however, retarded at HP because of reduced diffusivity of oxygen interstitials under pressure [11]. So at the applied HP–HT conditions there were created clouds of oxygen atoms, forming particles of sub-stoichiometric (as compared to stoichiometric SiO_2) composition. Most of created defects were too small to be detected by topography and TEM, so only some agglomerates of them were detected by mentioned methods on the 'background' of non-resolved numerous much smaller cloud-like defects. Such small defects did not emit, during their growth, enough silicon interstitials to create detectable dislocation loops nor the defects were large enough to create 'misfit-related' dislocations [2]. In other words, enhanced pressure of gas ambient during annealing of oxygen-containing silicon samples at 1400 K resulted in creation of much lower concentration of dislocations but of much higher concentration of small cloud-like oxygen clusters, in comparison to effect of the same annealing but at atmospheric pressure. The presence of such small defects (non-radiative recombination centres) in the Si samples annealed at atmospheric pressure and, especially, at HP, explains the absence of excitonic PL at 1.1 eV.

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