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Structure perfection variations of Si crystals grown by Czochralski or floating zone methods after implantation of oxygen or neon atoms followed by annealing

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Abstract. Structure perfection of the silicon crystals grown by the Czochralski and floating zone methods after implantation with oxygen or neon fast iones followed by annealing at the temperatures T ~ 1050-1150 ^{0}C, when large SiO_x precipitates were formed, was studied by means of various X-ray diffraction methods. Considerable increments of integral reflectivities for different Bragg reflections of such samples in comparison with those calculated for a perfect crystal were detected. Broadening of the spatial intensity distribution curves for the Bragg-diffracted beams taken by a single crystal spectrometer as well as the maps of the diffuse isointensity distribution near a reciprocal lattice point, registered by the Philips high-resolution diffractometer, are shown. All of these diffraction effects related to creation of the SiO_x precipitates formed on structural damages caused by implantation of oxygen or neon ions and subsequent annealing. Contrary to FZSi, where the appearence of SiO_x precipitates was discovered due to intensive diffuse scattering near the layer contained the implanted oxygen ions only, in the case of CZSi samples with larger concentration of oxygen (up to $1*10^{18}$ at/cm^3) such defects were formed not only near the burried layer, created by ions of oxygen or neon (with energy E = 4 MeV, dose 10^{14}cm^{-2}) but in a bulk of a crystal. Annealing of the FZSi crystals implanted by oxygen (E ~ 200 keV, dose ~ 10^{16}-10^{17} cm^{-2}) at enhanced hydrostatic pressure, additionally stimulated SiO_x precipitation close to the implanted layer.

Keywords: Czochralski and floating zone silicon, SiO_x precipitates, radiation damages, oxygen and neon ions, Bragg-diffraction of X-ray, reflectivity, Debye-Waller static factor.

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1. Introduction

The SiO_x precipitates surrounded by system of dislocation loops appearing in silicon crystals containing oxygen impurity due to solid solution decay at high temperatures play an important role as intrinsic gettering centres for cleaning active zones of semiconductor devices from undesirable impurities [1]. Usually, these defects are formed on various initial structure distortions (associations of various point defects) existing in as-grown crystals after preliminary low temperature treatment [2]. Structure distortions induced in crystals by irradiation with various particles (neutrons, atoms, electrons) of high energy or during technological processes of active impurity implantation can also play the role of such centres [3, 4]. Therefore, it is interesting to make clear an effect of implantation of silicon crystals with oxygen because just this impurity play an important role in creation of initial stages of large SiO_x precipitates. It is known [5] that the processes of SiO_x formation in a silicon containing oxygen can considerably change the integral characteristics of structure perfection of a crystal, namely: its reflectivity, the Debye-Waller factor, coeficient of extinction. Analysing character of these parameter variations, one can judge of the structural transformation in a crystal and determine the character of existing defects. The aim of this paper was the investigation of structure perfection variations in a crystal by means of different X-ray diffraction methods after annealing the samples implanted by accelerated ions of chemically active oxygen or neutral atoms (neon) having approximate masses. For this purpose, Si crystals grown by Czochralski and floating zone methods, containing different quantity of "grown-in" oxygen atoms, were used. Thus, the process of oxygen solid solution decay was investigated in the samples with radiation defects (with or almost without "grown-in" interstitial oxygen atoms).

2. Materials and methods

Three Si samples of the first series I, samples 1, 2, and 3, of (100) surface orientation and of thickness about 3,0 mm, containing rather high concentration C_0 of oxygen (up to ~ 10^{18} cm^{-3}) were grown by Czochralski method (CzSi). The samples 2 and 3 were irradiated with neon and oxygen ion beams of energy 4 MeV/u and dose 10^{14} particles/cm^2 from the Warsaw Cyclotron [6]. The implantation was performed by uniformly defocused beam at room temperature. The sample 1 was kept as a reference one. The implanted CzSi samples were next annealed at 1050 ^{0}C for 5h in the atmosphere consisting of argon (80 %) and oxygen (20 %) to create SiO$_x$ precipitates on the radiation damages. The annealed samples are noted as 1′, 2′ and 3′. Because of a large concentration of oxygen in CzSi, SiO$_x$ precipitates were formed not only near the surface subjected to irradiation but in the bulk of these crystals.

Six Si samples of the second (II) series, (1 - 6), were grown by the floating zone (FZ) method and had low oxygen concentrations (up to C_0 ~ 10^{16} cm^{-3}). All of them had (111) orientation and were subjected to implantation with oxygen ions of 200 keV energy and doses $10^{16} \div 10^{17}$ cm^{-2}. Local maximum concentration C_{0l} in the burried layer situated on the depth close to 0,4 μm (thickness Δt ~ 0.09 μm) was estimated to reach $4 \times 10^{21} \div 4 \times 10^{22}$ cm^{-3}.

Then the samples 1 - 6 of the second series were annealed at 1130 °C in the argon atmosphere using high hydrostatic pressure P (up to 12 kbar). It was done to promote the process of SiO$_x$ formation [7] in the near-surface layer containing implanted oxygen ions. The technological parameters of annealing of the FZSi crystals are given in the Table 1.

Structure perfection changes were investigated by means of a set of X-ray diffractometrical methods based on the Bragg case of diffraction [7]. For characterization of the structure state (appearence of distortions connected with defects) the increments ΔR_i of the measured integral reflectivities R_i for different Bragg diffraction maxima after various treatments (implantation with oxygen or neon ions or annealing), relatively to the values R_i^p, calculated for a perfect crystal, were used :

$$\Delta R_i = R_i - R_i^p = R_i^p L + 2LR_i^k . \qquad (1)$$

Here: R_i^k is the kinematical reflectivity for an ideal-mosaic crystal. Thus, analysing the ΔR_i increments, one could determine the static Debye-Waller factors L after

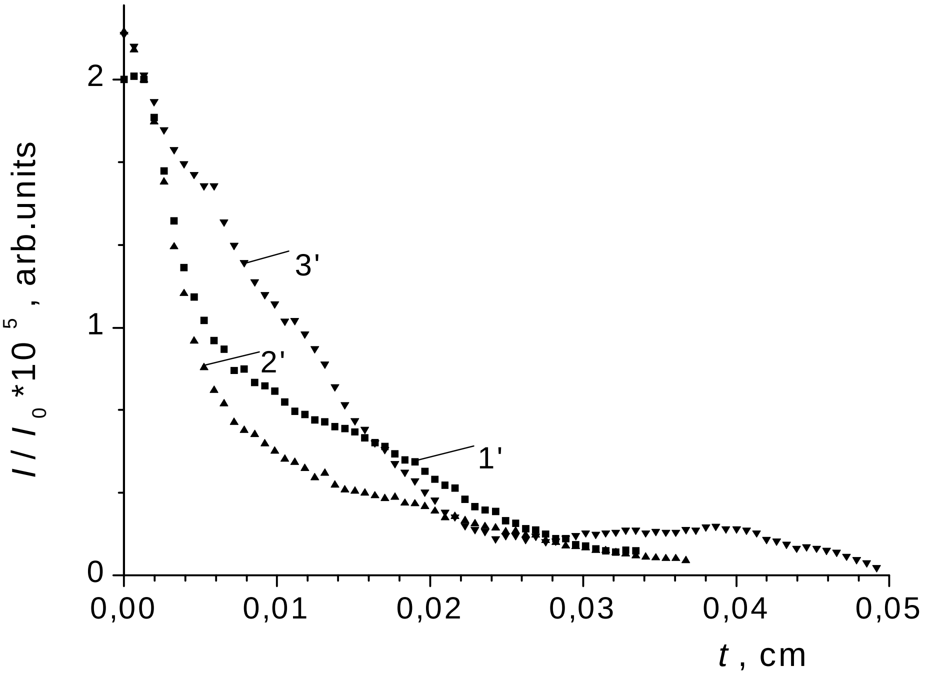

Fig. 1. Spatial intensity distributions (SID) of the Bragg diffracted beams of AgK$_\alpha$ radiation in the samples (the first series) after irradiation by high energy ions (E = 4MeV/u, dose 10^{14} particles/cm^2) and annealing (1050 ^{0}C, 5 h). Non-implanted sample – 1′, sample implanted with neon – 2′ and oxygen – 3′ ions.

Table 1. The technological parameters of annealing the FZSi samples (second series).

Number of the sample	Type of treatment	Ion dose (cm^{-2})	Annealing parameters (temperature, pressure, duration)
1	implanted only	10^{16}	-
2	implanted and annealed	10^{16}	1130°C,1 bar,10 h +1130°C,12 kbar,5 h
3	the same	10^{17}	1130°C,1 bar,5 h
4	the same	10^{17}	1130°C,12 kbar,5 h
5	the same	10^{16}	1130°C,6 kbar,5 h
6	the same	10^{16}	1130°C,1 bar,10 h

various treatments of the samples. More exact expression for the ΔR_i can be obtained from the De-Marco and Weiss formulae [8] which were successfully used for experimental data interpretation [5].

Additionally, the spatial intensity distribution (SID) of diffracted beams in a real space by single crystal spectrometer and two-dimensional maps of the diffuse intensity countors near the reciprocal lattice point were obtained by a Philips high-resolution diffractometer. The last method was used, however, for investigation of the FzSi only. Both of these methods permitted us to judge qualitatively the structural state of the samples.

3. Results and discussion

Let us start with discussion of the results obtained for samples of the first series. In Fig. 1 the SID as a function of the depth scattering, *t*, is presented. For the sample 3`

Table 2. Integral perfection characteristics of the first series samples, i.e., increments of reflectivities ΔR_i and Debye-Waller static factors L for as grown (1), irradiated (2, 3) and annealed (1′, 2′,3′) crystals measured for 220, 440, 660, 880 Bragg reflections of AgK_α radiation.

Number of the crystal	220		440		660		880	
	$\Delta R_i\ 10^7$	L_{220}	$\Delta R_i\ 10^7$	L_{440}	$\Delta R_i\ 10^7$	L_{660}	$\Delta R_i\ 10^7$	L_{880}
1	2,5	-	3,3	-	7,3	0.018	2,7	0.03
2	18,0	0.002	23,0	0.01	11,0	0.028	5,3	0.07
3	8,4	0.001	3,6	0.002	6,5	0.016	1,7	0.02
1′	121,0	0.01	48,0	0.02	20,0	0.05	4,2	0.05
2′	68,0	0.006	32,0	0.015	15,0	0.04	2,7	0.035
3′	156,0	0.013	67,0	0.032	23,7	0.06	4,4	0.056

Notes: The Czochralski grown Si samples: (1) – as grown, (2) – implanted with neon ions, and (3) – implanted with oxygen ions respectively. Figures 1′, 2′, 3′ designate the same crystals annealed at 1050 °C for 5 h. The depthes of X-ray penetrating in Si under the Bragg diffraction conditions (extinction length Λ) are equal to 50, 71, 120, 205 µm for 220, 440, 660 and 880 reflections of AgK_α radiation, respectively.

irradiated with the oxygen ions the noticeable broadening of the curve in comparison with those of the samples 1′ and 2′ is seen indicating more intensive X-ray diffuse scattering on the SiO_x precipitates formed during annealing just near the surface of the sample. One can see also less intensive tails of diffuse scattering for the samples 1′ and 2′. It means that during annealing the SiO_x precipitates were formed not only on the radiation damages created by the Ne ions, but also in the bulk of non-irradiated sample 1′.

The results of the reflectivity increment measurements after irradiation of the CzSi samples and their successive annealing are given in Table 2. An enhancement of the R_i is seen for the irradiated samples (2, 3) due to creation of distorted zones near the surface where the accelerated ions stoped. The most noticeable distortions were created in the case of the neutral neon atoms which did not interact chemically with the silicon matrix. For both of the samples 2 and 3 the largest ΔR_i changes were revealed for the Bragg reflections of low orders (220 and 440) for which the depths of diffraction maximum formation (extinction length, Λ) are equal 50µm and 71 µm, respectively. It may mean that the damaged zones affecting the ΔR_i changes were situated somewhere between the surface and these depths.

More drastic changes of the ΔR_i were discovered in the samples 1′, 2′ and 3′ of the first series after their annealing at 1050 °C for 5 hours, probably due to intensive SiO_x precipitates appearing. The largest R_i increment, $156 \cdot 10^{-7}$, characterises the sample 3′ irradiated with oxygen. This result is in agreement with the the SID for the the Bragg diffracted beam presented in Fig. 1 where the largest broadening of the curve 3′ is shown. So, one can suppose that the oxygen ions created higher local concentration of this impurity and, therefore, more favourable conditions for oxygen solid solution decay during annealing of the crystal as comparing with the case of neon ions.

Let us consider now the results obtained after annealing of the FZSi samples, implanted by oxygen (series II). At first we analyse peculiarities of the SID for the Bragg diffracted beams in the samples 1 - 4, presented in Fig. 2. The broadest curve corresponds to the sample 2 subjected not only to implantation with oxygen ions but annealings, too (see Table 1). Its large width is connected perhaps with strong diffuse scattering on SiO_x precipitates appeared during high temperature annealings. The other curves (e.g., 3 and 4), taken from the samples subjected to various annealings (of not so long duration as for the sample 2), are narrower. The peak value of the relative intensity I / I_0, is however, higher in the sample 2 than in as-implanted sample 1 due to contribution of diffuse scattering on SiO_x precipitates appearing in defects of complex annealing near 1130 °C.

The maps of two-dimensional distribution of diffuse scattering intensities near the 333 reciprocal point given in Fig. 3, confirm in general, the above interpretation of SID. Really, the as-implanted sample 1 of series II

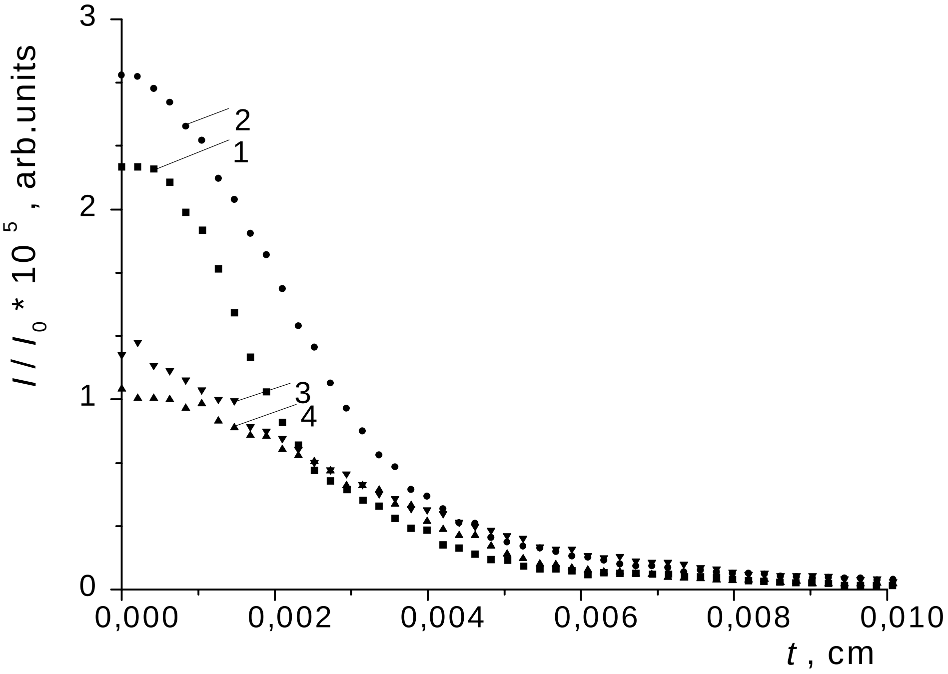

Fig. 2. Spatial intensity distributions (SID) variations for the samples of second series implanted with oxygen and annealed (symbols are given in Table 1). (1) sample implanted with oxygen only. I_0 is the intensity for incident beams.

(Fig. 3A) shows the existence of two reciprocal points (one of them relates to the upper thin (~ 0,3 μm) layer near the implanted surface). Subsequent annealing of the FZSi samples 2, 3 resulted in disappearing the discussed second point and in forming the broad pictures of diffuse scattering on SiO_x precipitates (Fig. 3C).

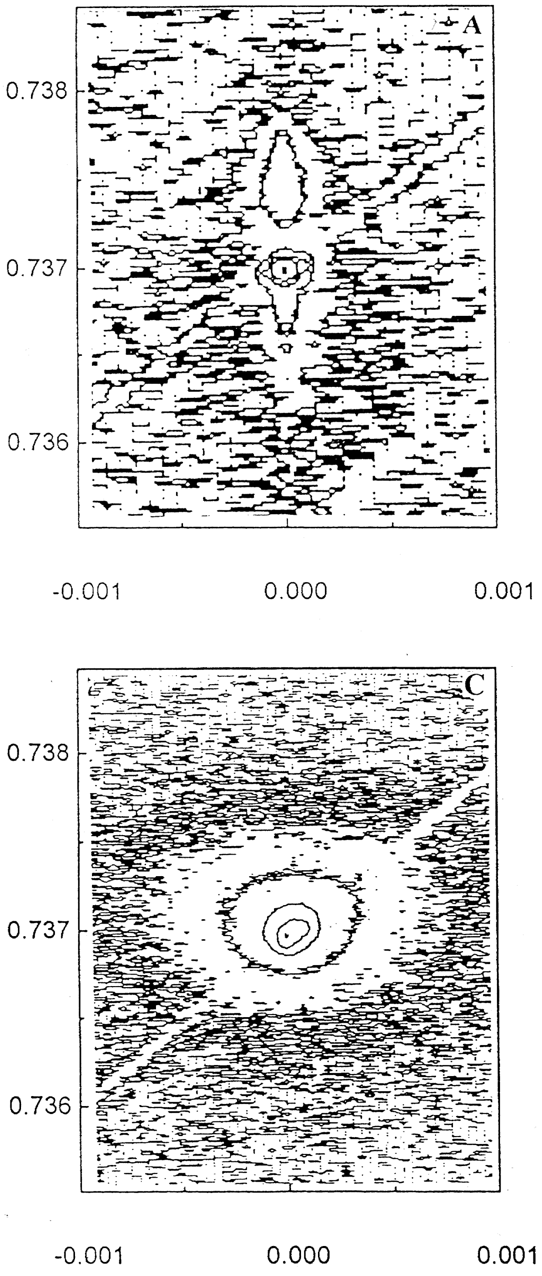

Fig. 3. Maps of the diffuse scattering taken near 333 reciprocal lattice point for $CuK_{\alpha 1}$ radiation in the samples of the II series subjected to implantation with oxygen ions of energy $E \sim$ ~ 200keV, dose 10^{16} - 10^{17} at/cm^2 and followed annealing (see table 1). The axes are marked in λ/2d units, where λ is wavelength and d interplanar distance.
A – after implantation with O only (dose 10^{17} cm^{-2}),
C – implanted with O, dose 10^{16} cm^{-2} and annealed at 1130°C, 1 bar, 10 h + 1130 °C, 12 kbar, 5 h.

Now let us discuss the curves of the integral reflectivity increments ΔR_i versus a diffraction vector H taken for the 111, 333, 444, 555, and 777 Bragg reflections in the samples 1 - 6 of the second series after various treatments (Fig. 4.). Besides these curves, the dotted graph for the extinction length Λ (the depth of diffracted beam penetration) as a functoin of H is also given for relative comparison with the depth of scattering. It can be seen that the main changes in scattering process occured just for the low orders (111 or 333) reflections. It means that the process of oxygen solid solution decay takes place just closely to the implanted layer where the local concentration C_{01} of oxygen could reach level of 10^{21} or 10^{22} at/cm^3.

The sample 1 of the second series is characterised by very high increment of reflectivity, ΔR_i, for the 111 reflection (curve 1 in Fig. 4). The reason of such large changes in R_i in this sample consists mainly in elastic bending a crystal [9] due to presence of the oxygen burried layer near the implanted surface. Thus, for this sample, the Debye-Waller factor, L, hardly could be calculated from the formula (1). Annealing of the sample 2 (see Table 1) resulted in more considerable increment of ΔR_i than that of the sample 1 due to appearence of SiO_x precipitates closely to implanted zone and in relaxation of elastic strains. For this sample the volume part of SiO_x precipitates r_0, being estimated from the value of ΔR_i ($r_0 \approx 2L = 0{,}036$), is the largest among the other crystals because this sample was annealed for 15 h in total at 1130 °C and additionally it was treated under high pressure (P = 12 kbar).

Concerning an influence of high pressure on the ΔR_i increments (Fig. 4), the results for the samples 3 and 4

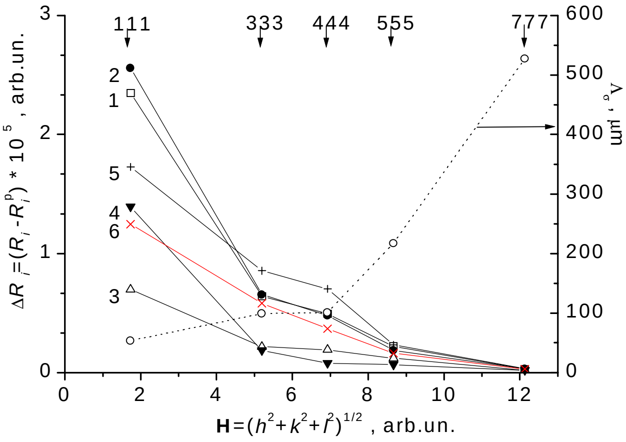

Fig. 4. Integral reflectivity increments ΔR_i versus the diffraction vector **H** ~ $(h^2 + k^2 + l^2)^{1/2}$ for the FZSi crystals after implantation with oxygen and annealing. The numbers of samples correspond to those in Table 1.

should be compared. It is easy to see that $\Delta R_i(4) > \Delta R_i(3)$ because the first of them was annealed during the same time (5 h) but under higher pressure (P = 12 kbar). So, creation of SiO_x precipitates has been more noticeably manifested under an influence of hydrostatic pressure. The same conclusion could be drawn from comparison of the ΔR_i for the samples 5 and 6 ($\Delta R_i(5) > \Delta R_i(6)$), though the time of treatment was longer for the sample 6. However, comparing the increments of R_i for the samples 2 and 4 treated under pressure p = 12 kbar by the same time (5 h) one can conclude that $\Delta R_i(2) > \Delta R_i(4)$ because the first of these samples was annealed additionally for 10 h, though this preannealing was carried out at ambient pressure (P = 1 bar).

4. Conclusion remarks

Structure perfection of the Czochralski grown silicon crystals and of silicon crystals obtained by floating zone method subjected to implantation of oxygen and neon ions and then to annealing at the temperatures, where intensive silicon-oxygen solid solution decay takes place, was studied. Noticeable changes of the increments of integral reflectivities for the Bragg diffracted beams of the hard X-ray radiation and considerable broadening of the spatial intensity distribution curves as well as maps of isointensive diffuse countors near a reciprocal lattice point after the mentioned annealings of both types of crystals in comparison with a perfect crystal were established. Contrary to FZSi, where intensive diffuse scattering caused by appearance of SiO_x precipitates near the oxygen-implanted layer was detected only, in the case of CZSi those defects were formed not approximately to the damaged layer but through the bulk. Preferential creation of SiO_x precipitates was discovered, however, near the zone of radiation damages caused by high energetic ions of neon and oxygen, especially in the last case. One can suppose that chemically active impurity introduced in silicon matrix creates more favourable conditions for following appearence of SiO_x precipitates at high temperatures.

It was shown that annealing of the implanted FZSi crystals at enhanced hydrostatic pressure in argon atmosphere additionally stimulated the diffuse scattering intensity due to formation of the mentioned precipitates during process of oxygen solid solution decay close to the implanted layer. Changes of character different diffraction phenomena are better displayed after such treatments. These changes manifest themselves more distinctly under higher hydrostatic pressure.

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