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Influence of hydrostatic pressure at the temperatures about 1500 K on defect structure of Czochralski silicon

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Abstract

The averaged values of radii $\bar{r}$ and concentration $\bar{n}$ of microdefects which are the SiO_x precipitates surrounded by dislocation loops were determined from the measured X-ray integral reflectivities of Czochralski grown silicon crystals subjected to annealing at high hydrostatic pressure (10^7–10^9 Pa) as well as from analysis of differential diffuse scattering behaviour near the Bragg angle. The values of these parameters and the Debye–Waller static factor behaviour show that process of the SiO_x dissolution which usually takes place at the temperatures about 1500 K is slowed down in condition of hydrostatic pressure as comparing with treatment of such samples about 1500 K but by atmospheric pressure ($P=10^5$ Pa). © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Defects of various types in Si crystals grown by Czochralski method (CzSi) with high concentration of oxygen (up to 1×10^{18} cm^{-3}) appear not only during growth of an ingot but also after its further thermal treatments. One of the defect types are SiO_x precipitates and connected with them dislocation loops. These imperfections play an important role of effective sinks for undesirable impurities and point defects, which can change considerably the electrical parameters of semiconductor materials [1]. Therefore, investigation of these defects is of interest from the scientific and practical point of view.

Effect of high temperature treatment under pressure (HTP) on formation and evolution of the oxygen precipitates has been studied in [2–5]. Quantitative parameters of structure imperfection, i.e. the Debye–Waller static factor, L, and additional absorption coefficient, μ_d, due to diffuse scattering of X-rays on defects were determined from analysis of the integral reflectivities, R_i, of the Laue diffracted beams of X-rays. The HTP was shown [2] to have an influence on generation of new defects. Such treatment can also lead to dissolution of SiO_x precipitates and connected with them imperfections. As a result of treatment at ≈1500 K in condition of hydrostatic pressure the former crystal perfection can be restored but not to so great extent comparing with heating of such sample at the mentioned temperature in argon atmosphere [3]. The aim of this paper was investigation of the hydrostatic pressure influence on evolution of the parameters of microdefects (the average radii and concentration) in the temperature region, where the dissolution of these imperfections may occur.

2. Experimental details

Dislocations-free CzSi crystals grown in [100] direction were investigated. The oxygen concentration in them was close to 1×10^{18} cm^{-3}. Before the measurements all of the samples were previously heated at two temperatures (1000 K for 20 h and 1320 K during 20 h) noted as T_1, where the oxygen solid solution decay takes place and the high concentration of microdefects connected with SiO_x precipitates (surrounded by a system of dislocation loops [1]) could appear. The imperfection level of all of the samples after preannealing was considered as an initial state of a crystal structure. After above mentioned preannealing one series of the samples (2–4) was annealed at the tempera-

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Table 1
Technological parameters of the HTP treatment of the CzSi crystals in the temperature interval of the oxygen precipitates dissolution[a]

Sample number	Series of samples	Thickness t (μm)	Pressure P (Pa)	Temperature T (K)	Time of annealing (min)
1	Initial state	530	–	–	–
2	1	495	10^5	1580	5
3	1	456	10^7	1580	5
4	1	440	10^9	1580	5
5	2	507	10^5	1620	30
6	2	464	10^7	1620	30
7	2	391	10^9	1620	30

[a] All of the samples were previously annealed at 1000 K for 20 h and at 1320 K for 20 h (initial state).

ture $T_1 = 1580$ K during 5 min and second one (5–70) was treated at $T_2 = 1620$ K for 30 min to dissolute the mentioned defects at conditions of the hydrostatic pressure (Table 1).

The main characteristics of microdefect structure,obtained by the first method, are the mean concentration $\bar{n}_1$ and effective radius $\bar{r}_1$ of microdefects which are connected with the L and μ_d characteristics of structure perfection [6]:

$$L = 8\bar{n}_1 \bar{r}_1^{9/2} (\beta H)^{3/2},$$
$$\mu_d = 8\pi^2 \bar{r}_1 L \Lambda^{-2} \cos^2\theta \tag{1}$$

where H, Λ, θ and β stand for the diffraction vector, extinction length, Bragg angle and a constant value close to 0.01 respectively. The L and μ_d parameters were determined by analysis of the experimental data of reflectivities R_i^{exp} and by using of the values R_i^{p} calculated for a perfect crystal with in the approximations of a thin ($\mu t \sim 1$) and a thick ($\mu t > 6$) crystal [7,8]. Here μ and t are the photoelectric coefficient of absorption and a thickness of a sample respectively. Besides, information about the values of $\bar{r}_2$ was also obtained by investigation of the differential diffuse scattering intensity I_{DS} as a function of the angle deviation parameter $\Delta\theta$ from the exact Bragg position of a sample [6,9] (the second method):

$$q_0 = H\,\Delta\theta\,\cos\theta = e^{1/2}/r_2 \tag{2}$$

Determination of the r_2 value is possible, as it was shown in [10], in the angular region, where the transition from the Huang regularity $I_{DS} \sim q^{-2}$ to the law intensity $I_{DS} \sim q^{-4}$ takes place (Fig. 1). Parameter q characterizes deviation of the angular position of measurement from a reciprocal lattice point. The values e and q_0 in Eq. (2) stand respectively for the base of the natural logarithm and value of q, obtained at intersection of the graph of the I_{DS} with abscissa axis. The measurements of the integral reflectivities R_i for the 220 and 440 Laue reflections were carried out on the same sample using the CuKα ($\mu t > 9$) and AgKα ($\mu t < 1$) radiations. So the L and μ_d parameters could be determined from the R_i using the corresponding formulas obtained in the thick or thin crystal approximations of the dynamical theory [8]. Measurements of the angular distribution of the diffusely scattered intensity I_{DS} near the 400 reciprocal lattice point were carried out using the double crystal spectrometer adjusted in the (n, $-m$) Bragg position for CuKα radiation.

3. Results and discussion

Dependences of the L and μ_d parameters on value of the hydrostatic pressure P for the samples of both series are given in the Table 2. The values of the P and T for these samples are given in the Table 1. One should note that the sample 1 (the initial state) has rather damaged structure because the $L \approx 5 \times 10^{-2}$ value testifies to large quantity of defects ($\bar{n} \sim 5.9 \times 10^{10}$ cm^{-3}). Treatment of the sample 2 at temperature 1580 K even for 5 min resulted in noticeable

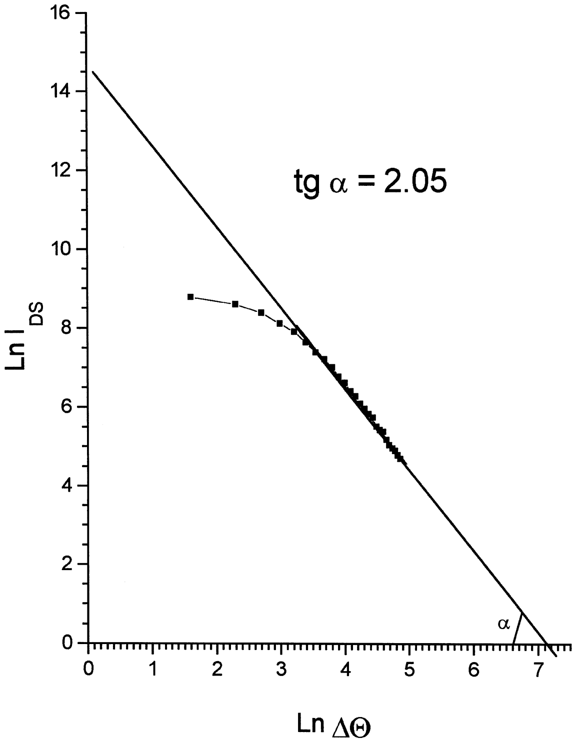

Fig. 1. Plot of the integral diffuse scattering logarithm versus logarithm of the angular deviation $\Delta\theta$ of the sample 1 position from the exact Bragg case in the Huang region (tg α = 2.05) taken in the initial state (Table 1). 400: reflection of CuKα radiation. $\Delta\theta$ was measured in seconds of arc.

Table 2
Values of the $\bar{n}$, $\bar{r}$ parameters of microdefects calculated from the reflectivities R_i by the formula (1) in Refs. [6] and [7] as well as obtained by analysis the angular dependence of the I_{DS} [10]

Sample number	Reflectivity $R_{i(220)}$ for CuKα	Reflectivity $R_{i(440)}$ for AgKα	μ_d (cm^{-1})	L	$\bar{r}_1$ (Å)	$\bar{n}_1$ (cm^{-3})	$\bar{n}_1 \cdot \bar{r}_1^{9/2}$ (cm$^{3/2}$)	$\bar{r}_2$ (Å)
1	1.47×10^{-7}	1.04×10^{-5}	6.3	4.7×10^{-2}	690	5.9×10^{10}	3.5×10^{-13}	1400
2	1.04×10^{-6}	2.34×10^{-6}	9.9	4.9×10^{-3}	10 390	3.1×10^{4}	3.7×10^{-14}	1690
3	7.59×10^{-7}	2.90×10^{-6}	9.5	7.6×10^{-3}	6440	4.1×10^{5}	5.7×10^{-14}	1500
4	1.19×10^{-6}	3.70×10^{-6}	11.4	1.1×10^{-2}	5150	1.7×10^{6}	8.5×10^{-14}	1370
5	1.57×10^{-6}	1.35×10^{-6}	11.7	1.4×10^{-3}	11 110	2.5×10^{4}	4.1×10^{-14}	1570
6	1.76×10^{-6}	2.70×10^{-6}	13.0	4.7×10^{-2}	10 320	4.2×10^{4}	4.9×10^{-14}	1460
7	6.60×10^{-7}	7.90×10^{-6}	10.3	4.9×10^{-3}	15 800	0.3×10^{4}	2.5×10^{-14}	1600

improving of its structure (see the values of L and $n_1 \cdot r_1^{9/2}$ parameters comparing with initial state. Average radius r_1 has grown by this though the concentration of microdefects, n_1, decreased on several orders of value. Annealing of the samples 2–4 of the first series at the 1580 K during 5 min by enhancement of pressure from 10^5 to 10^9 Pa caused: (i) a considerable increase of the L value, and (ii) enhancement of the diffuse absorption due to scattering on defects. So the structure perfection of the samples has deteriorated judging from increase of the $\bar{n} \cdot \bar{r}^{9/2}$ parameter from 3.7 to 8.5×10^{-14} cm$^{3/2}$. At the same time the effective radius $\bar{r}_1$ of microdefects, calculated by means of the system of Eq. (1) has grown in the sample 2 (till≈10 400 Å after annealing at 1580 K and P=10^5 Pa) comparing to the initial state ($\bar{r}_1 \approx 690$ Å). The rise of r_1 may be explained perhaps by absorption of small microdefects by large ones. One can note in the samples (2–4) of the first series a further increase of the L and μ_d parameters and therefore the corresponding variations of the microdefect structure parameters by increasing of the hydrostatic pressure. These variations of the $\bar{r}$ and $\bar{n}$ under action of a pressure characterize a considerable deterioration of the structure perfection of the sample 4 as comparing with the sample 2 (see the changes of the $\bar{n} \cdot \bar{r}^{9/2}$ parameter).

A similar situation, but more clearly expressed, is observed in the samples 5–7 of the second series obtained from another ingot which were annealed for a longer time.However they had possibly another defect structure in its initial state.

The analysis of the slope K of the dependence ln(L) on ln ($\Delta\theta$) [6] shows that the predominate type of defects is the large precipitates or dislocation loops because $K \approx 2$ (Fig.1). The typical average radii $\bar{r}_2$ determined from the q_0 values obtained by extrapolation of the $I_{DS} = (\ln q)$ function to the intersection point with the abscissa axis (Fig. 2) are given in Table 2. Comparing the $\bar{r}_1$ and $\bar{r}_2$ values ($\bar{r}_1 = 690$ Å and $\bar{r}_2 = 1400$ Å), we consider that the values of the effective radii of microdefects in initial state of the samples as determined by two independent methods are close to each other (at least the same order of magnitude). One can note that the $\bar{r}_2 = 1400$ Å is also close to the value of this parameter $r = 2200$ Å determined in [10] after the similar annealing of such Si crystals. With enhancement of the pressure level P one can note a certain disagreement in defect dimensions as obtained by two methods though the tendency of their behaviour is preserved. The possible reason of the discrepancy consists perhaps in a larger contribution of big microdefects to the diffusely scattered intensity in the angular region situated close to the Bragg position. Such imprefections of a structure do not influence essentially the behaviour of the $I_{DS} = f(\ln \Delta\theta)$ function.

The microdefects of other dimensions discovered by means of two independent methods in the samples, treated under hydrostatic pressure, their evolution confirm the established tendency of the defect structure variations [3].Some improvement of the crystal structure and suppression of this process under pressurization takes place.

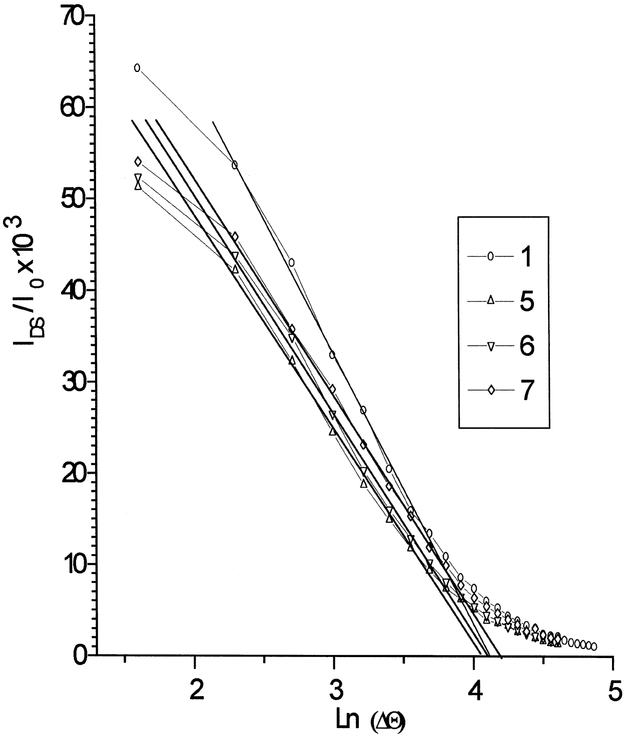

Fig. 2. Plot of the integral diffuse scattering intensities I_{DS} normalised to the primary beam intensity I_o versus the ln($\Delta\theta$) for the samples 1, 5, 6, 7. The values $q_{01} = 1.152\times10^{-3}$ µm, $q_{05} = 0.978\times10^{-3}$ µm, $q_{06} = 1.099\times10^{-3}$ µm, $q_{07} = 1.206\times10^{-3}$ µm were calculated from Eq. (2).

The analysis of the defects radii behaviour with change of the hydrostatic pressure values for the samples of the first series suggests a partial dissolution of discussed microdefects under pressurization. Parallel process of new microdefects creation may probably take place too, because their concentration increases (see the sample 4 in the Table 2). The first process, i.e. annihilation of small microdefects by interaction them with large ones, predominated perhaps in the samples of the second series which were treated under hydrostatic pressure for longer time.

4. Conclusions

Investigations of structure imperfection of CzSi crystals, carried out by the two independent X-ray methods, after annealing the samples in condition of pressurization show that the hydrostatic pressure may slow down the process of disappearing of the microdefects connected with oxygen precipitation in the region of retrograde dissolution (≈1500 K). This process demonstrates itself more distinctly by increasing of temperature and time of treatment. Combination of different independent X-ray methods for defect structure investigations allowed us to obtain the relatively close meanings of the microdefects radii in an initial state of samples, i.e. $\bar{r}_1$ and $\bar{r}_2$, and to establish the microdefects of different dimensions appearing under hydrostatic pressure.

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