STUDYING THE DECAY KINETICS OF AN OXYGEN SOLID SOLUTION IN Cz–Si SPECIMENS AT THEIR SQUEEZING

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Three-crystal X-ray diffractometry (TCD) was used to study the decay kinetics of an oxygen solid solution in silicon crystals grown by the Czochralski method (Cz–Si) and subjected to squeezing. The squeezing stress applied to specimens in the course of their isothermal annealing was found to enhance the decay rate of an oxygen solid solution in Cz–Si.

1. Introduction

Stresses are known to affect the processes of decay of supersaturated solid solutions. Depending on the stress sign and the dimensions of impurity atoms, they can either accelerate or slow down the decay processes [1], as well as the processes of donor center formation in the course of ion implantation [2]. Pressure substantially enhances the generation of vacancies and divacancies in silicon; it reduces the energy of their formation by forcing atoms with dangling bonds to come closer to one another and by increasing the exchange interaction between them [3]. Literature data testify that, at the annealing of silicon, the rate of reduction of the optically active oxygen concentration, which is associated with the diffusion coefficient of oxygen atoms, becomes more than two orders of magnitude higher at temperatures of 500–900 °C and pressures of about 10^9 Pa [4]. The growth of diffusion coefficient should evidently accelerate the precipitation of oxygen-containing inclusions. Such a conclusion follows unambiguously, if one considers the dependence of the critical radius of a precipitate on the temperature [5]. The relevant relation includes the coefficient of elastic stress, which diminishes the critical radius at the squeezing (here, the critical radius corresponds to a threshold, when the oxygen precipitate dimensions start to grow at the annealing of crystals). Hence, the compressive pressure applied to specimens would enhance the decay rate of a solid solution of oxygen in silicon and, respectively, increase the dimensions of oxygen-containing precipitates formed at that. To answer the question whether this hypothesis is true, we studied the process of formation and growth of oxygen-containing precipitates in Cz-silicon, when the latter was annealed at a constant temperature. In the course of annealing, the specimens were deformed within their elastic range by the four-support bending method. Such a technique enabled us to study both the squeezed and stretched sides of the specimen.

2. Specimens and Experimental Technique

Specimens were cut out from KEF-4.5 Cz–Si wafers polished at a plant. The oxygen content in them was about 10^{18} cm^{-3}. Their thickness was 0.7 mm, width 3 mm, and length about 2 cm. The working surface corresponded to plane (111), and it was additionally chemically polished after every annealing. Specimens were isothermally annealed for 30 h at 600 °C in air. The detection of formed oxygen precipitates and the determination of their dimensions and concentration were fulfilled by analyzing the integral intensity of the diffusion peak in three-crystal x-ray diffraction patterns [6]. The stress at the external surface of specimens was created by means of the four-support bending; it was found to amount to 52.7 MPa. Crystals were annealed, when the stress was being applied.

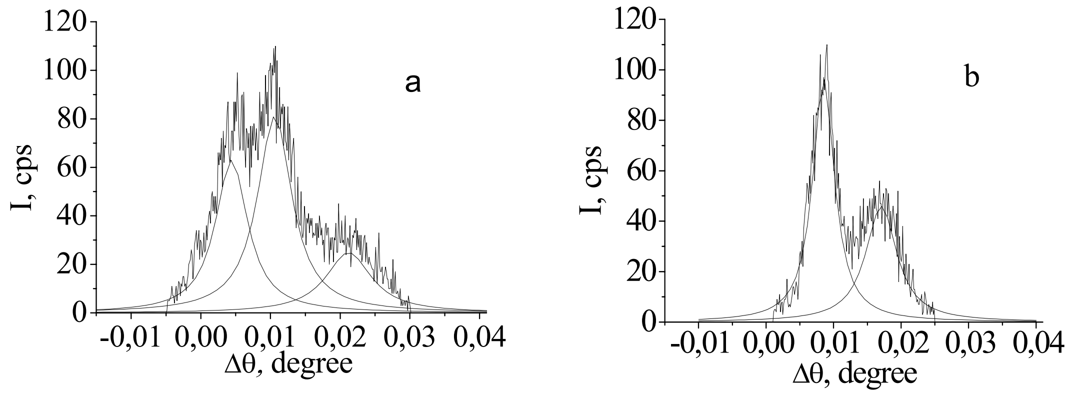

Fig. 1. Diffraction patterns for the squeezed (a) and stretched (b) sides of the crystal. Thermal annealing for 15 h; $\alpha \approx 30''$

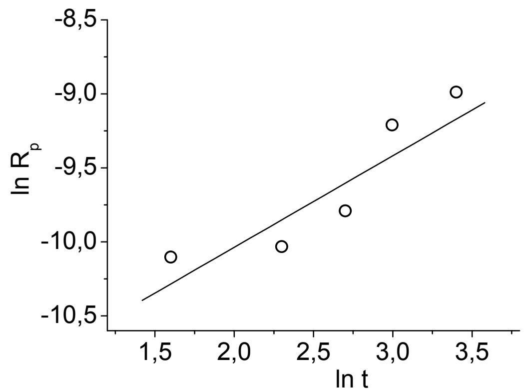

Fig. 2. Dependence of the precipitate radius (in cm units) on the annealing time (in h units) on the log-log scale

3. Experimental Results and Their Discussion

The analysis of diffraction patterns obtained in the $\theta - 2\theta$ mode demonstrated, first of all, that they had a usual three-peak profile, with the intensities of diffusion, main, and side maxima being sufficient for treatment. In diffraction patterns for crystals annealed at 600 °C but not subjected to external strains, the diffusion peaks were not observed. The latter were also not fixed on the stretched side of stressed specimens. At the same time, at the squeezed side of specimens, diffusion peaks of x-ray radiation scattering were clearly seen (Fig. 1). This evidenced for the presence of processes related to the decay of the oxygen solid solution in squeezed Cz–Si specimens at their annealing already at 600 °C. The comparison of specimens annealed isothermally for different time intervals enabled us to determine the dimensions and the concentration of formed precipitates and, by analyzing the growth of precipitate dimensions in time, to calculate the diffusion coefficients of oxygen in crystals. Specimens were annealed for 5, 10, 15, 20, and 30 h. Following the technique reported in work [6], we monitored the variations of the integral diffusion peak intensity as a function of the specimen deviation angle from the Bragg position to calculate the dimensions and the concentration of emerged oxygen-containing precipitates. The relevant data are quoted in Table. One can see that the growth of annealing time gives rise to an increase of precipitate dimensions and a reduction of their concentration. Proceeding from general considerations for diffusion processes, the temporal growth of the characteristic dimension of a precipitate R_P, which is a geometrical mean between a plane and a spherical one, should satisfy the formula [6]

$$R_{\rm P}^{2,7} = 4,19 \times 10^2 \Delta n_0 V_0 ({\rm Dt})^{3/2}.$$

Hence, $\ln R_P$ has to change proportionally with the variation of $\ln t$, if the oxygen supersaturation concentration Δn_0 and the volume per one oxygen atom V_0 are constants. The indicated dependence does take place (Fig. 2). Then, adopting the values $\Delta n_0 \approx 5 \times 10^{17}$ cm^{-3} and $V_0 \approx 50$ Å^3, the slope of the obtained straight line can be used to estimate the oxygen diffusion coefficient. We obtained the value of about 2.6×10^{-12} cm^2/s, which is two to three orders of magnitude higher than the standard values for this quantity at a temperature of 600 °C ($10^{-14} \div 10^{-15}$ cm^2/s [7]). Hence, the squeezing of specimens enhances the oxygen diffusion

Time variation of the dimensions and the concentration of precipitates at a temperature of 600 °C

t, h	$R_{\rm P} \times 10^5$, cm	$c_{\rm P} \times 10^7$, cm^{-3}
5	4.1	8.2
10	4.4	62.3
15	5.6	19.5
20	10	0.24
30	12.5	0.14

in them, which is not observed under the action of tensile stresses.

By discussing the results obtained, we note that there are a few works in the literature, where, making use of that or another method (mainly, the optical ones), an anomalously high mobility of oxygen atoms in silicon was registered at annealing temperatures 350–500 °C [8]. It arose after the silicon crystals with oxygen supersaturation were subjected to certain physical influences (for instance, a preliminary heat treatment, uniform squeezing, *etc.*). The reasons why the enhanced diffusion emerges are unknown, but a possibility for a mobile structural unit, which includes oxygen, to exist in silicon is discussed in the literature. In particular, the matter is that oxygen can exist in two states: as a part of quasimolecules Si–O–Si and as free interstitial atoms. It is clear that the mobility of oxygen atoms in the latter case is considerably higher [8]. Uniform squeezing of crystals under definite conditions probably transfers some oxygen atoms from the first to the second state. An assumption can be made that the compressive stress acts analogously in our case as well. The efficiency of such a transition of oxygen atoms evidently depends on the temperature, the magnitude of applied stress, and some other external factors (e.g., the annealing environment, irradiation, probably – the time duration of loading, *etc.*). Those issues are still to be studied.

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ВИВЧЕННЯ КІНЕТИКИ РОЗПАДУ ТВЕРДОГО РОЗЧИНУ КИСНЮ В ЗРАЗКАХ Cz–Si ПРИ ЇХ СТИСНЕННІ

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Р е з ю м е

Методом трикристальної рентгенівської дифрактометрії проведено дослідження кінетики розпаду твердого розчину кисню та виявлено зміни у кінетиці при стисненні зразків кремнію, вирощеного методом Чохральського (Cz–Si). Було виявлено, що прикладене до зразків стискаюче напруження під час ізотермічного відпалу прискорює розпад твердого розчину кисню в кремнії.