STUDY OF THE INFLUENCE OF A HIGH TEMPERATURE TREATMENT ON THE DISPERSION OF X-RAYS BY DEFECTS GENERATED IN CRYSTALS Cz-Si

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By triple-crystal diffractometry, we study the dispersion of X-rays by Czochralski-grown silicon crystals with local defects appeared in them during the annealing at temperatures of 850—1000 °C and the repeated annealing at 1050 °C. The characteristics of admixture-structural complexes are calculated. A method of calculation of the radii and densities of clusters and dislocation loops and a method of diagnostics of the defects' type are proposed.

1. Introduction

At present, the structural diagnostics of various materials is an important physico-technical problem, and large collectives of scientists are working in this direction. A significant place in the arsenal of instrumental methods of the research of real crystals belongs to X-ray diffraction analysis and diffractometry.

The analysis of data derived with the use of these methods is based on the dynamical theory of dispersion, whose various versions were thoroughly developed, in particular, by the scientists of Institute of Metal Physics of NASU. As one of the most successful experimental methods of study of the X-ray dispersion by weakly distorted crystals with randomly distributed defects, we mention triple-crystal diffractometry, within which the diffusive and coherent components of dispersion can be immediately determined. Therefore, it is widely used for the registration and study of various, mainly local, structural imperfections.

This trend of studies includes a great number of scientific works, in which the authors were able, by processing the experimental data within the dynamical theory of X-ray dispersion, to estimate the diffraction-related and direct physical characteristics of dispersion centers such as their concentration, sizes, etc. Since a result derived in the given method depends on the type of a chosen model, there arises the necessity to compare X-ray diffraction data with the results of direct observations, for example, with the use of electron microscopy [1, 2].

Accordingly, our purpose was the elaboration of a new method of calculation of defects' parameters and its application to the research of the influence of a preliminary heat treatment of silicon crystals on the X-ray dispersion by created structural-admixture complexes.

2. Procedure of Measurements and Calculations. Results of Researches

Measurements were conducted on Czochralski-grown silicon specimens. The heat treatment was executed in two stages according to the method proposed in [1]. On the first stage, specimens were held at 850, 900, 950, and 1000 °C for 5 h. On the second stage, they were repeatedly annealed at 1050 °C for 24 h.

After each stage, we registered X-ray Bragg diffractograms on the $CuK_{\alpha 1}$ emission on a semiautomatic triple-crystal diffractometer under the symmetric reflection from surface (111) of specimens upon their turn from the Bragg position by an angle α from 10 to 100″ with an interval of 5″. The permanent intensity of radiation was supported in all cases, that falls like $I_0 \approx 10^5$ imp/s.

Prior to the analysis of the diffractometry data, we needed to choose a model which would be in the best

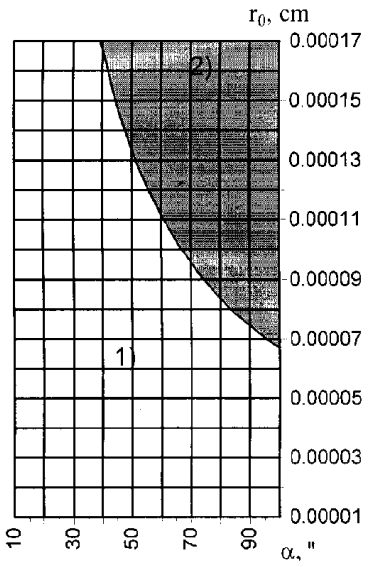

Fig. 1. Graphic representation of the limits of a realization of cases *1* and *2* for relation (1)

correspondence with the experiment conditions and a type of defects, whose parameters should be determined. As the starting point, we take the intricate function $J(k_0)$ describing the intensity of diffraction maxima for the different types of defects in the whole interval of deviation angles θ of the analyzer from the Bragg position. According to works [3—5],

$$J(k_0) = \begin{cases} b_2 \ln\left(\frac{ek_m^2}{k_0^2}\right) + b_3\left(\frac{k_0^2}{2k_m^2} - 1\right), & k_c \le |k_0| \le k_m, \\ \left(b_2 - \frac{b_3}{2}\right)\frac{k_m^2}{k_0^2}, & |k_0| \ge k_m. \end{cases} \quad (1)$$

Here, $k_0 = \frac{2\pi}{\lambda}\alpha \sin 2\theta_{\rm B}$, $k_m = \frac{2\pi}{r_0}$, $k_c = 2\pi/\Lambda_\sigma$, λ is the radiation wavelength, r_0 is the mean radius of defects, Λ_σ is the extinction length, and $\theta_{\rm B}$ is the Bragg angle. In order to specify a model and, respectively, the formulas, we made to attempt estimate the limits of the first and second versions of relation (2.) [3]. Since $\Lambda_\sigma^{(111)} = 4.73{\cdot}10^{-4}$ cm and $\lambda_{{\rm Cu}K\alpha_1} = 1.541{\cdot}10^{-8}$ cm for silicon, we have $k_c > k_0$ already at $\alpha > 12''$. So, for the first version of (1), the inequality $|k_0| - k_m \le 0$ is satisfied, which is equivalent to $\left|\frac{2\pi}{\lambda}\alpha \sin 2\theta_{\rm B}\right| - \frac{2\pi}{r_0} \le 0$. The graphical representation of this inequality as a function of the radius of defects and the deviation angle of a specimen is given in Fig. 1.

Thus, the first version must be realized at relatively small α and r_0, whereas the second corresponds to the region of micron sizes of the dispersion centers. Respectively, the dependences of the integral width of a diffusion maximum on α will be different in both cases [6]. Upon the transition from region 1 to region 2 (Fig. 1), this dependence must change from the U-like to a quickly falling one with increase in α. All this enables us to choose a model for the implementation of necessary calculations using the primary experimental data. Our experiment meets the first version of relation (1). At the same time, the long-term high-temperature annealing of specimens, when the micron-size dispersion centers appear, is described by the second version of (1) [3].

The intricate functions, b_2 and b_3, of the Bragg angle and the Poisson ratio are written in [3] for the cases where the dispersion centers are clusters or dislocation loops. The substitution of proper numerical values of the parameters in the above-presented expressions leads to the following relation:

$$J(k_0) = A\left(BR^2\alpha^2 - \ln R\alpha - C\right). \quad (2)$$

Here, $A = 0.84B_K$, $B = 2.081 \times 10^{14}$, and $C = 17.18$ for clusters, and $A = 4.6B_D$, $B = 4.252 \times 10^{13}$, and $C = 16.84$ for dislocation loops. The values of B_K and B_D were calculated in [7, 8]. In the case of a mixture of spherical and planar clusters, $B_K \approx 3.59 \times 10^{39} r_0^{5.4}$. For the dislocation loops, $B_D = 3.46 \times 10^{30} r_0^4$.

The functions $J(k_0)$ appear, as multipliers, in the following expressions for the integral intensity R_Σ and half-width w_α of the diffusion maximum of a diffractogram:

$$R_\Sigma(\alpha) = \frac{cC^2E^2m_0J(k_0)}{2\mu_0}, \quad (3)$$

$$w_d = \frac{\sin 2\theta_{\rm B} J(k_0)}{B_0}\alpha. \quad (4)$$

In formulas (3) and (4), c is the concentration of dispersion centers, C is the polarization factor, E is the Debye—Waller static factor, m_0 is a constant equal to 0.169 cm^{-1} for reflection (111), μ_0 is the linear coefficient of photoelectric absorption, and $\theta_{\rm B}$ is the Bragg angle.

Assume that the first term in the parentheses in (2) is much less than the two subsequent ones, which is characteristic of small values of $r_0\alpha$. Then the plot of R_Σ vs $\ln\alpha$ must be linear, and its extrapolation to $R_\Sigma = 0$ enables us to estimate the sizes of dispersion centers as

$$r_0 = e^{-(\ln\alpha_0 + C)}, \quad (5)$$

where α_0 is the abscissa of the intersection of an extrapolation line (we used the least-squares method) with the $\ln\alpha$ axis of the plot.

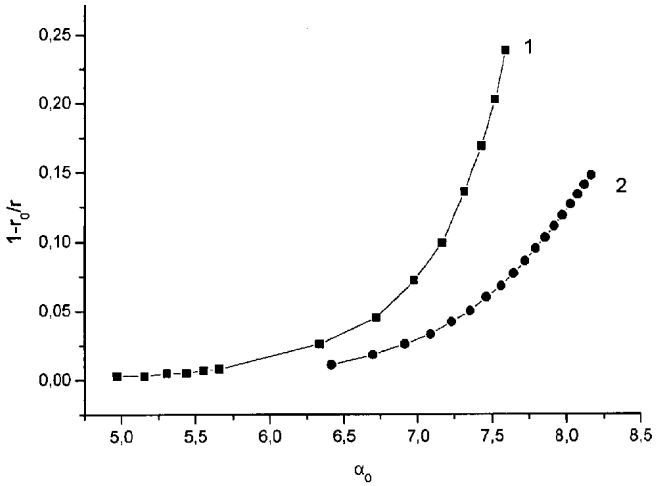

Fig. 2. Dependences of the relative errors of the calculation of the radii for clusters (1) and dislocation loops (2)

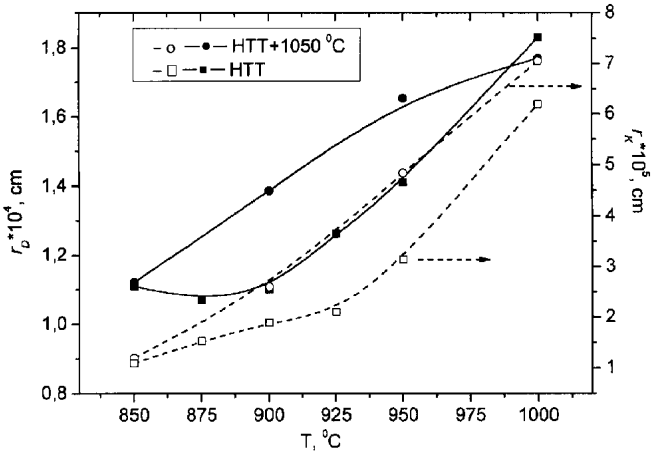

Fig. 3. Radii of dislocation loops r_D (continuous curves) and clusters r_K (dashed ones) vs the heat treatment temperature

To be sure in the correctness of the interpretation of results, it is necessary to estimate the error of such a calculation of r_0, i.e., to estimate the contribution of the first term. This can be done theoretically through the construction of the corresponding dependences $J\,(k_0)$ on $\ln\alpha$ with and without regard for the squared term and the calculation of, respectively, the values of r_0 and r. We note that the theoretical curves were built for α_0 from 20 to 90″. In such a way, we constructed the relative errors of calculations of the radii of defects, $\frac{r-r_0}{r}$, vs α_0 (Fig. 2). Equation (2) was solved numerically with the Mathematica 5.0 software.

As seen in Fig. 2, the error of calculations of r_0 without regard for the squared term is greater for clusters and can reach from 1 to 24 %.

We note that, by extrapolating the dependence of R_Σ on $\ln\alpha_0$, it is possible, in principle, to simultaneously determine the radii of two (or even more) types or different radii for one type of defects. In this case, we may separate, more or less precisely, two rectilinear sections with different slopes on the corresponding curves and to derive two points of the crossing of the extrapolating lines and the abscissa axis.

A diffusion peak carries the main portion of the information about the imperfect structure of a specimen. Its integral intensity is determined by relation (3) and is a power function of the radii of dispersion centers. Therefore, the intensity of diffusion dispersion practically equals to zero even at large concentrations c of dispersion centers already at $r \approx 10^{-6} \div 10^{-7}$cm. Thus, the given method is more sensible to the defects of greater radii in the case of a wide range of the size of defects.

The above-described variant of calculations of the sizes of dispersion centers with the use of the integral intensity of a diffusion peak can be applied to the case where $R_\Sigma(\alpha)$ is defined by the X-ray dispersion intensities from dislocation loops, $R\,(\alpha)_D$, and from the clusters of admixture atoms, $R\,(\alpha)_K$. Since $R_\Sigma\,(\alpha) = R\,(\alpha)_D + R\,(\alpha)_K$, it is possible to select the values of r_D, r_K, and c_D/c_K. The quantities r_D and r_K calculated by such a method are presented in Fig. 3 for various conditions of heat treatment.

The presence of the well-pronounced main peak on diffractograms allows us to determine the static Debye—Waller factor L and its change under different conditions of annealing by the method described in [6]. The nonmonotone behavior of L as a function of the temperature of heat treatment is shown in Fig. 4. We see the clear minimum at a temperature of annealing of about 900 °C. Beginning from just this temperature, we observe a growth of the ratio c_D/c_K, which indicates that the processes related to the formation of dislocation loops begin to dominate (Fig. 4). The further annealing of all specimens at 1050 °C leads to a sharp growth of the concentration of dislocation loops in them.

Works [7—9] present a method of calculations of the concentrations of defects with the use of the static Debye—Waller factor. In the case of clusters, we have [10]

$$L = \begin{cases} \frac{1}{2} c_K n_0 \eta^2, & \eta^2 << 10, \\ c_K n_0 \eta^{3/2}, & \eta^2 >> 10, \end{cases} \qquad (6)$$

where $n_0 = \frac{V_P}{v_c}$ is the number of elementary cells in the precipitate volume $V_P = \pi r_K^2 h_p$, $\eta = \alpha_0 n_0^{\frac{1}{3}} a_0 \frac{H}{2\pi}$, $\alpha_0 =$

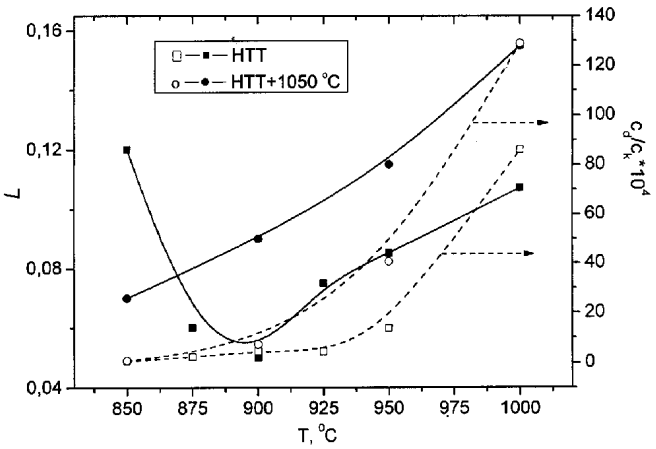

Fig. 4. Static Debye—Waller factor L (continuous curves) and relation c_D/c_K (dashed ones) vs the heat treatment temperature

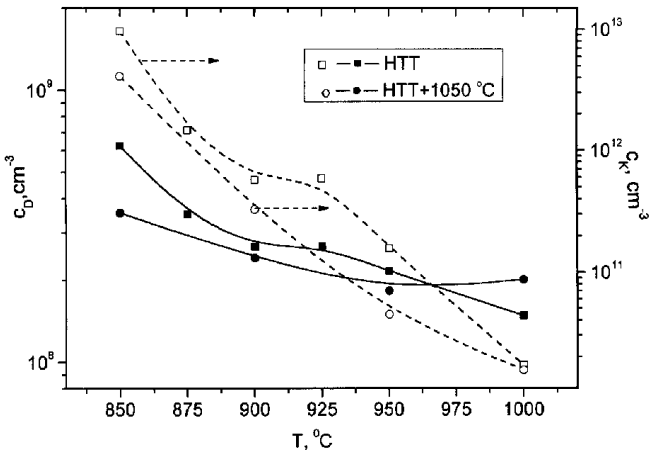

Fig. 5. Concentrations of dislocation loops (continuous lines) and clusters (dashed ones) vs the heat treatment temperature

$= \Gamma\varepsilon\left(\frac{3\pi^2}{4}\right)^{\frac{1}{3}}$, $h_p = a_1 r_P \left(\frac{L}{r_P}\right)^{a_2}$, a_1 =3.96; a_2 =0.597; ε=0.0242; a_0 is the lattice constant, $\Gamma\approx$0.6; and $N = 2\times10^8\text{cm}^{-1}$.

For the clusters with the sizes calculated above, the second of Eqs. (6) must be satisfied. So, let us assume that the Debye—Waller static factor is the sum of the appropriate values of the mean squared displacements of atoms from the equilibrium positions due to the presence of dislocation loops and clusters in a specimen. Then we have

$$L = L_D + L_K. \tag{7}$$

In view of [3, 11], relations (6) and (7) yield

$$L = \frac{2c_D\Lambda_\sigma^2 C^2 m_0 J_D(0)}{\pi^2 \sin^2\theta_B r_{D_0} a_D} + c_K n_0 \eta^{3/2}. \tag{8}$$

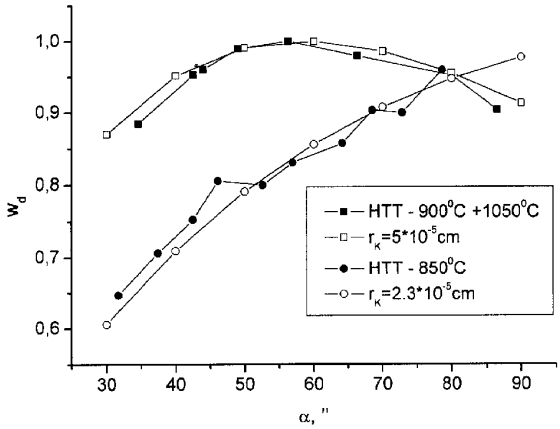

Fig. 6. The experimental and theoretical (constructed by fitting) dependences of the diffusion peak half-width on the turn angle of an analyzer

As seen from formula (8), the first and second terms depend on the concentration of defects. If the ratio of concentrations c_D/c_K is known, we can calculate their values. The derived values of concentrations are used in the construction of the plots in Fig. 5.

The author of work [1] presented the results of the studies of defects by electron microscopy, which were formed in specimens undergone a heat treatment similar to our one, namely the sizes and concentrations of precipitates after a previous heat treatment. By comparing the results given in Figs. 4 and 5 and the data in [1], we conclude about their agreement.

In conclusion, we note that, for the determination of a type of defects which give the main contribution to the dispersion of X-rays and define its parameters, it is possible to use the method of analysis of the dependence of the half-width of diffusion peaks on the specimen turn angle $w_d(\alpha)$ (4), where B_0 =0.03016·B_K for clusters and B_0 =1.86·B_D for dislocation loops. In this case, we must pay attention to that the ratio of the half-widths w_K/w_D is large. That is, clusters induce considerably wider diffusion peaks than dislocation loops. So, the summary half-width of a diffusion peak must be mainly determined by the presence of clusters. Dislocation loops give only an insignificant additional widening, which causes a reduction of the radii of clusters calculated by formula (4). To check up this supposition, we made attempt to fit the radius of clusters by (4) with the help of a computer so that the experimental curves of the half-width of a diffusion peak vs the turn angle of a specimen α were adjusted to the theoretical ones

(Fig. 6). As seen, the radii of clusters determined by such a method are approximately twice less than those obtained with the use of the integral intensities of diffuse maxima.

3. Conclusions

We have proposed a new method of both the diagnostics of the type of defects and the calculation of their radii and concentrations in view of the character of changes in triple-crystal diffractograms during the process of thermal decay of the hard solution of oxygen in silicon. We have found the radii and concentrations of clusters and dislocation loops, which arise as a result of different variants of the thermoannealing of Czochralski-grown crystals.

The comparative estimation of the methods of calculations of the parameters of centers of the dispersion of X-rays is carried out.

We have found a minimum on the plot of the Debye—Waller static factor vs the temperature of heat treatment, which is observed near a temperature of 900 °C. It is related, probably, to the features of temperature changes of the concentrations of defects. Namely after this temperature, the ratio c_D/c_K begins to rapidly increase, that is, the processes of multiplication of dislocation loops are intensified.

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ВИВЧЕННЯ ВПЛИВУ ВИСОКОТЕМПЕРАТУРНОЇ ОБРОБКИ НА РОЗСІЯННЯ РЕНТГЕНІВСЬКИХ ПРОМЕНІВ ДЕФЕКТАМИ, ЩО УТВОРЮЮТЬСЯ В КРИСТАЛАХ Cz-Si

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Р е з ю м е

Методом трикристальної дифрактометрії досліджено розсіяння рентгенівських променів вирощеними методом Чохральського кристалами кремнію з локальними дефектами введеними в них у процесі відпалу при температурах 850—1000 °C та повторного відпалу при 1050 °C. Розраховано характеристики домішково-структурних комплексів. Запропоновано метод обчислення радіусів і концентрацій кластерів і дислокаційних петель, а також метод діагностики типу дефектів.