STUDY OF LIGHT SCATTERING PROCESSES IN SILICON SINGLE CRYSTALS WITH NONHOMOGENEOUS DISTRIBUTION OF IMPURITIES

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UDC 621.315.592
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The origin of the nonmonotonous behavior of small angle light scattering (SALS) observed for single crystals of Si after the transition of oxygen impurity atoms into an electrically active state as a part of thermodonors (TDs) has been analyzed. It has been shown that both the rise and the fall of the SALS intensity during the thermal treatment of the Si samples at 450°C resulted from the formation of TD microclusters at the places of initial microfluctuations of the oxygen concentration. The analysis of the experimental data has allowed us to evaluate numerically the local concentration of TDs in the clusters of various sizes.

Introduction

The light scattering in semiconductor crystals results mainly from the fluctuations of the electron part of the dielectric permittivity ε

$$\delta\varepsilon = \frac{\varepsilon(r) - \langle\varepsilon\rangle}{\langle\varepsilon\rangle} = \frac{4\pi e^2}{mk^2c^2}\Delta n(r), \qquad (1)$$

where m is the conduction electron mass, $k = 2\pi/\lambda$, λ is the light wavelength in the crystal, $\Delta n(r)$ is the deviation of the electron density from its average value in the bulk of the specimen, c is the speed of light. If the spatial dimensions a of such fluctuations are much bigger than the light wavelength ($a \gg \lambda$), the forward scattering, i.e. at small angles, mainly occurs. To define parameters characterizing the spatial dimensions of the structural defects, the SALS method is used (see, e.g., [1–3]). Oxygen is distributed nonuniformly in the bulk of Si crystals. Due to their electroneutrality, such concentration fluctuations practically do not affect the dielectric permittivity variation. Nevertheless, they can be charged making use of the thermal treatment at high temperature. It is known (see, e.g., [4]) that the thermal treatment at 450 °C of the Si specimens grown by Czochralski method results in creating TDs which are oxygen complexes. The diffusion coefficient of oxygen atoms in Si at 450 °C is very small ($\sim 10^{-19}$ cm^{2}s^{-1}). Therefore, the TD spatial localization slightly differs from that of the oxygen atoms in an initial crystal. The TD generation rate is proportional to the cubic power of the oxygen concentration [5]. So, the TD generation is to be expected within the oxygen "clouds" [3] where the oxygen concentration exceeds the averaged one. In this case, the nonhomogeneity degree of the TD distribution would be increased by orders in comparison with the oxygen nonhomogeneity. At the places of oxygen clouds, the clusters of TDs are to appear. The TDs were ionized at room temperature [3] at which the measurements were carried out. Therefore, those clusters induce the electrical nonhomogeneities in the bulk of the crystal, which can essentially affect the light scattering processes.

1. Light Transmission Features in Crystals with Nonhomogeneities

Since the fluctuations of the oxygen distribution in Si have a wide range of spatial dimensions with various oxygen concentrations in fluctuations, the nonhomogeneous distribution of TDs appeared during the thermal treatment will also have the wide spectrum

of both the spatial dimensions of the TD clusters and the TD concentrations in them. The nonhomogeneities of a size $a \gg \lambda$ scatter the light mainly forward, while the nonhomogeneities of a size less than the light wavelength will contribute to the isotropic scattering. The nonhomogeneities of both types affect not only the scattering features but diminish the intensity of the incident light in the initial direction and in the directions of scattering as well.

In the case of the thin ensemble of nonhomogeneities, the intensity of the scattered wave is equal to the product of the incident wave intensity, the nonhomogeneity density $\rho(\mathbf{r})$, the scattering cross-section $\sigma(\mathbf{r})$, and the path length l of the light in the crystal. It corresponds to the single-scattering model. This model can be applied if the optical path $\tau = \int \rho(\mathbf{r})\ (\sigma_a(\mathbf{r}) + \sigma_s(\mathbf{r}))\ ds \ll 1$, where σ_s and σ_a are the total cross-sections for the scattering and absorption, respectively, and the integration is carried out along the path of the light transmission s. According to [6], an allowing for the multiple scattering becomes necessary as early as at $\tau \sim 0.1$. In our experiments, as is shown by the estimations quoted below, $\tau \sim 1$.

The general equations of the light transmission theory in nonhomogeneous media taking into account the multiple scattering [4] can be obtained making use of the analysis of the relation between the intensities of the scattered (diffuse), $I_d(\mathbf{r},\mathbf{s})$, and incident, $I_{ri}(\mathbf{r},\mathbf{s})$, waves.

In the course of the light transmission through the crystal, the intensity of the former, $I(\mathbf{r},\mathbf{s})$, decreases due to the scattering by the value $\rho\sigma I ds$, and increases by the value $\int \rho\sigma_d(\mathbf{s},\mathbf{s}')I(\mathbf{r},\mathbf{s}')ds'$ as a result of the scattering of a part of the light intensity $I(\mathbf{r},\mathbf{s}) = I_{ri}(\mathbf{r},\mathbf{s}) + I_d(\mathbf{r},\mathbf{s})$, which irradiates the given volume from other directions s', in the s direction. In the first approximation of the theory of multiple light scattering in nonhomogeneous media [4], the diffuse intensity can be written as

$$I_d(\mathbf{r},\mathbf{s}) = \int_0^s \exp\left\{-\left(\int_0^s \rho\sigma_d ds - \int_0^{s'} \rho\sigma_d ds\right)\right\} \times$$

$$\times \rho \int \sigma_d(\mathbf{s},\mathbf{s}')I(\mathbf{r},\mathbf{s}')ds', \qquad (2)$$

where σ_d is the differential scattering cross-section.

As a rule, the intensity of scattered waves is essentially less than that of the incident wave, so when obtaining the approximate solution of the integral equation (2), the iteration method can be used in the integral of its r.h.s. The first approximation gives $I(\mathbf{r},\mathbf{s}) \approx I_{ri}(\mathbf{r},\mathbf{s}) \approx I$. In this case, the diffuse intensity

$$I_d = I \sum_j l\rho_j\sigma_{dj} \exp\left(-\sum_i l\rho_i\sigma_i\right). \qquad (3)$$

This expression was obtained in suggestion about the statistical homogeneity of the specimen. In Eq. (3), the summation is carried out over each j-th site possessing the differential scattering cross-sections σ_{dj} which correspond to small-angle and isotropic scattering. To put it differently, this expression describes the situation where the summary intensity of the scattered light is measured. In the exponent power, the total scattering cross-sections of all sites are included, irrespective of the relation between the wavelength and the spatial dimensions of sites.

The formulae for the differential scattering cross-sections in the approximation $\delta\varepsilon/4\pi \ll l$, i.e. in the case where the field inside a nonhomogeneity slightly differs from the applied one, can be derived by the conventional method [7,8]:

$$\sigma_d = 0.5\pi\gamma k^4 V^2 \Phi_\varepsilon(\mathbf{q}). \qquad (4)$$

In Eq. (4), V is the volume of the crystal where $\delta\varepsilon(\mathbf{r}) \neq 0$ and k is the wave vector length. The nonhomogeneity of $\varepsilon(\mathbf{r})$ is quantitatively characterized by the function

$$\Phi_\varepsilon(\mathbf{q}) = V^{-1} \int \langle\varepsilon(\mathbf{r})\varepsilon(0)\rangle e^{i\mathbf{qr}} d\mathbf{r}, \qquad (5)$$

where $\mathbf{q} = 2\mathbf{k}\sin(\theta/2)$, θ is the angle between the wave vectors of the incident and scattered waves. In this case, $\gamma = 1 - \sin^2\theta\ \cos^2\theta$.

The scattering cross-section value is determined by the correlation function $\psi_\varepsilon(\mathbf{r}) = \langle\delta\varepsilon(\mathbf{r})\delta\varepsilon(0)\rangle$ which depends on a specific model of nonhomogeneities. For example, for the case of the light scattering by a sphere of radius a with the relative dielectric constant $\delta\varepsilon$, which is constant over the nonhomogeneity volume [8], into the solid angle ω,

$$\sigma_d = \frac{k^4 a^6}{18}(1 + \cos^2\theta)\varphi^2(qa),$$

$$\varphi(qa) = \frac{3}{(qa)^3}(\sin(qa) - (qa)\cos(qa)). \qquad (6)$$

For $ka \gg l$, the function $\varphi^2(qa)$ deviates noticeably from zero only in the narrow angle interval $\theta \leq l/ka$.

In this interval for the total scattering cross-section, we obtain

$$\sigma_s = \frac{\pi k^2 a^4 (\delta\varepsilon - 1)^2}{18} \text{ for } a \gg \lambda,$$
$$\sigma_s = \frac{k^4 a^6 (\delta\varepsilon - 1)^2}{3} \text{ for } a \ll \lambda. \quad (7)$$

Thus, the scattering cross-sections depend differently on the spatial dimensions of the inclusion and the wavelength in accordance with the relationship between them.

In the Si crystal, there are nonhomogeneities in the oxygen atom distribution and the relevant fluctuations in the TD distribution. As a result, the spatial fluctuations of the charge carrier distribution function $n(\mathbf{r})$ in the crystal appear. Due to the conservation law of the electroneutrality $\int\limits_V [N_{\rm TD}(r) - 2n(r)]\, dV = 0$, the distribution of free charge carriers will approximately correspond to that of TDs. For the sake of simplicity, we adopt the step-like character for this distribution.

The parameters which determine the intensity of a diffuse wave are the TD cluster volume V, the cluster density ρ, and the TD density Δn in a cluster. According to Eq. (1), it is the latter parameter that governs the value of the dielectric constant in a cluster.

The TD clusters have spatial dimensions both larger and smaller than the probing light wavelength λ. Correspondingly, the micrononhomogeneities with the spatial dimensions $a > \lambda$ will contribute to the small-angle scattering, and the micrononhomogeneities with $a < \lambda$ give rise to the isotropic one. Moreover, taking into account the multiple scattering, both types of nonhomogeneities decrease the intensity of the diffuse wave.

In the framework of the applied approximations, the differential scattering cross-section equals

$$\sigma_d = \frac{\pi}{16} k^4 a^6 (\gamma_n n_{\max})^2, \quad (8)$$

where $\gamma_n = 4\pi e^2/mk^2c^2$. This expression is valid irrespectively of the relationship between the scale a of the nonhomogeneity and the wavelength λ. For the total cross-sections of the scattering by micrononhomogeneities possessing the spatial dimensions $a_1 > \lambda$ and $a_2 < \lambda$, we obtain

$$\sigma_1 = \frac{\pi^2}{18} a_1^4 k^2 (\gamma_n n_{1\,\max})^2,$$
$$\sigma_2 = \frac{\pi}{3} k^4 a_2^6 (\gamma_n n_{2\,\max})^2, \quad (9)$$

respectively. As a result, the principal formula (3) for the relative diffuse intensity can be rewritten as follows:

$$I_0 = l\Big(\frac{\pi}{16} k^4 \rho_1 a_1^6 (\gamma_n n_{1m})^2 + \frac{\pi}{16} k^4 \rho_2 a_2^6 (\gamma_n n_{2m})^2\Big) \times$$

$$\times \exp\Big(-\Big(\frac{\pi}{18} k^2 \rho_1 a_1^4 (\gamma_n n_{1m})^2 + \frac{\pi}{3} k^4 \rho_2 a_2^6 (\gamma_n n_{2m})^2\Big) l\Big). \quad (10)$$

Here, a_1 and a_2 are the spatial dimensions of nonhomogeneities of the first and second types, respectively, $n_{1\,\max}$ and $n_{2\,\max}$ are the relevant maximal values for the concentration of free electrons in those nonhomogeneities, ρ_1 and ρ_2 are the concentrations of the relevant nonhomogeneities. Making use of this expression for the intensity of light scattered at small angles and comparing it with the experimentally measured one, it is possible to estimate the concentration of the i-th TD clusters and the averaged, over the volume, carrier concentrations caused by those TDs.

2. Experiment

The SALS measurements were carried out according the procedure described in detail elsewhere [1, 5]. The Si specimens of the dimensions $30 \times 30 \times 2$ mm were used. The concentrations of the oxygen and carbon impurities were determined by IR-adsorption measurements and constituted $9 \cdot 10^{17}$ cm^{-3} and less than $5 \cdot 10^{16}$ cm^{-3}, respectively. Totally 10 specimens have been thermally treated at 450 °C in the dry nitrogen environment during 20 to 250 hours. The angle dependence of the scattered light intensity $I(\theta)$ was measured for treated and control specimens, where θ is the angle between the direction of the probing beam of light with a wavelength of 10.6 μm in vacuum, and the observation one. The experimental dependence $I(\theta)$ was extrapolated to the zero angle.

In Fig. 1, the dependences of the normalized scattering intensity I_0 on the thermal treatment time at 450 °C are depicted. At first, the I_0 value increases essentially as the $t_{\rm tr}$ increases, attains the maximal value at $t_{\rm tr} = 25$ h, then drastically decreases, and becomes close to the initial value at 50 h. When $t_{\rm tr}$ increases further, the value of I_0 increases greatly again.

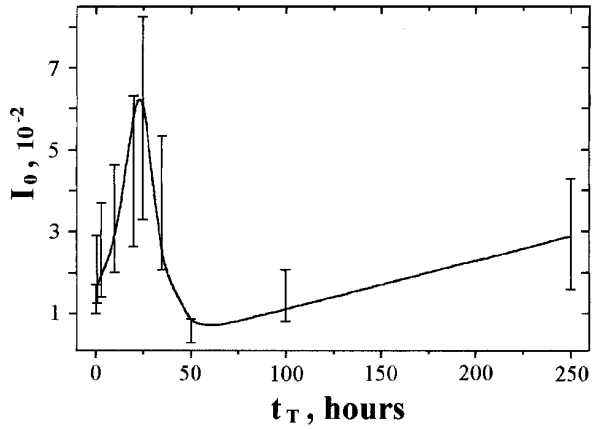

Fig. 1. Dependence of the normalized intensity I_0 on the thermal treatment time t_{tr} at 450 °C. Solid line is the theoretical curve [Eq. (10)]. The dispersion of the I_0 values stems from the multiple measurements at different specimen points

The specimen annealing at 520 °C during 30 min results in the disappearance of the maximum in the $I_0(t_{tr})$ dependence. The monitoring over the TD accumulation during the thermal treatment at 450 °C and their annealing at 520 °C was carried out by use of the temperature dependence measurements of the Hall effect in the interval 40–300 K. In Fig. 2, the typical dependences of the free electron concentration on the reciprocal temperature are shown for specimens with various t_{tr}. We see that those dependences have two regions of the electron concentration variation (40–100 and 125–200 K) which correspond to the charge inversion of two TD electron levels in the Si energy gap. From the temperature position of those regions and the curve slopes, the ionization energies of the relevant levels were determined. It occurred that, when t_{tr} arises, they vary between $E_c - (0.05 \div 0.07)$ eV and $E_c - (0.12 \div 0.16)$ eV. Those data are well consistent with the known data on the energy levels of oxygen TDs in Si [3]. For the initial dependences (before the thermal treatment), it is typical that there exists only one region of the charge inversion which corresponds to the ionization energy of the sulphur impurity donor level ($E_c - 0.04$ eV). The absence of other peculiarities in the temperature dependences of the electron concentration allows us to believe that the electric properties of the specimens under investigation are governed by the sulphur impurity in the initial crystal and by the oxygen TDs after the thermal treatment at 450 °C.

In Fig. 3, the dependence is shown of the variation $\Delta n = n_{tr} - n_0$ of the free electron concentration on the thermal treatment time, where n_0 and n_{tr} are the

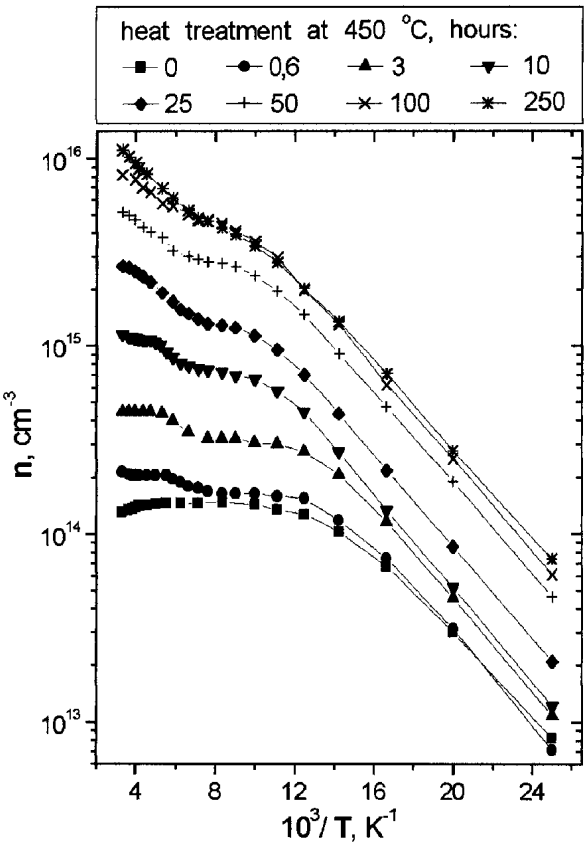

Fig. 2. Temperature dependences of the electron concentration in specimens with various t_{tr} at 450 °C

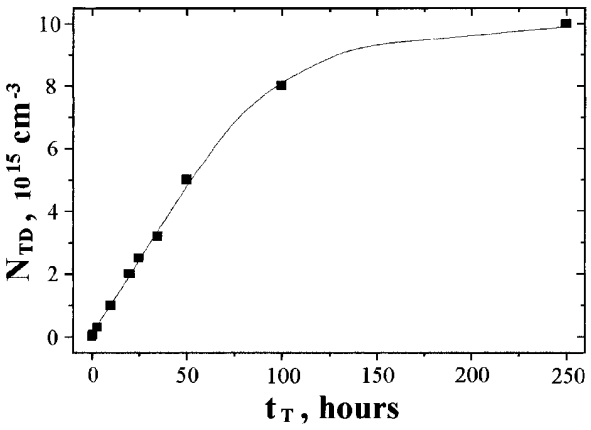

Fig. 3. Dependence of the thermal donor concentration N_{TD} on t_{tr} at 450 °C

electron concentrations at 300 °C before and after the thermal treatment. It has a view which is typical of the

kinetics of the TD accumulation at 450 °C. As is seen, up to $t_{\rm tr}$ = 100 h, Δn, being equal to the double TD concentration, increases linearly with $t_{\rm tr}$.

It is known [3] that the annealing at 520 °C results in the disappearance of the TDs appeared at 450 °C. In particular, during the 30-min annealing at such a temperature, almost 80% of the TDs created within 25 h of the thermal treatment at 450 °C lose their electrical activity. This correlates with the disappearance of the maximum in the SALS dependence (Fig. 1), which may evidence for the connection between TDs and the rise of the SALS intensity during the thermal treatment at 450 °C. But the question arises, why, providing the monotonous increasing of the TD concentration, the dependence of I_0 on $t_{\rm tr}$ is nonmonotonous?

3. Analysis of Experimental Data

We do not consider the size distribution of nonhomogeneous regions, and, for simplicity, we assume that there are only two types of nonhomogeneities with averaged characteristics. In larger nonhomogeneities, where the condition $a_1 > \lambda$ holds, the oxygen concentration $N_{\rm O}$ slightly deviates from the value obtained by averaging over the volume [5]. Therefore, the rate of the TD generation in those regions is small. So one should expect the linear dependence of the TD numbers on the thermal treatment time:

$$N_{\rm TD}a_1^3\rho_1 \approx n_{1m}a_1^3\rho_1 = A_1(1 + A_2t_{\rm tr}). \qquad (11)$$

For the regions where $a_2 < \lambda$, the dependence of the value $N_{\rm TD}a_2^3\rho_2$ on $t_{\rm tr}$ saturates rather quickly (in comparison with regions of the first type) due to the oxygen atom exhausting in them. Such a situation is well approximated by the probability integral $\Phi(t_{\rm tr}/t_0)$, with t_0 corresponding to the minimum in the experimental curve (Fig. 1):

$$N_{\rm TD}a_2^3\rho_2 = A_3\Phi(t_{\rm tr}/t_0). \qquad (12)$$

Making use of the specifically created computer program, in accordance with Eq. (10) and taking into account Eqs. (11) and (12), the intensity of the scattered light was calculated. The fitting parameters were A_1, A_2, and A_3 as well as ρ_1 and ρ_2.

In Fig. 1, a theoretical curve (solid line) is shown for the parameter values (see Table) giving the best fit to the experiment.

Let us consider results obtained with the help of Eq. (10) and depicted in Fig. 1. For $t_{\rm tr} < 25$ h, the concentration of the generated TDs is not enough to affect the exponent power in Eq. (10). The exponent power remains small and the exponent itself is almost equal to unity. Hence, the relaxation of the light intensity governed by the exponential factor in Eq. (10) is practically negligible. The SALS intensity increases along with the TD concentration (the pre-exponential factor). In this case, the increasing of the scattered light intensity results from the increasing of the TD concentration in the regions of both types.

For $t_{\rm tr}$ in the interval from 25 to 50 h, the TD concentration becomes enough to reduce the power of the exponent in Eq. (10) and hence I_0. Moreover, as the computer simulation shows, the contribution of the larger size nonhomogeneities ($a > \lambda$) to the exponent is insignificant. The relaxation of the scattered light intensity stems from the small size nonhomogeneities, where the TD concentration grows more quickly. In experiment, the fall of the I_0 value is observed until $t_{\rm tr}$ (50 h) when the TD generation in those regions ceases.

For $t_{\rm tr} > 50$ h, the TD concentration in small regions does not change (the saturation), i.e. the exponent in Eq. (10) remains constant. Therefore, there is no further relaxation of the light intensity. With $t_{\rm tr}$ increasing, the rise of the SALS intensity is observed only due to the increasing of the TD concentration in larger regions. This situation corresponds to a smaller slope of the curve in Fig. 1.

The obtained parameter values (see Table) make it possible to estimate the averaged, over the volume, concentration of the free electrons $\Delta n = \rho_i a_i^3 n_{i\,\max}$ which is induced by TDs generated in the volumes of the i-th nonhomogeneities. For example, at $t_{\rm tr}$ = 100 h, we have $\Delta n_1 = 8{\cdot}10^{14}$ cm^{-3} in the case of nonhomogeneities with $a_1 \gg \lambda$ (in Si, $\lambda = 3.1$ μm) and $\Delta n_2 = 9{\cdot}10^{15}$ cm^{-3} for $a_2 \ll \lambda$. On the basis of the averaged values obtained for concentrations which are induced by large and small TD microfluctuations, one may evaluate the local TD concentrations. Assuming $a_1 > 3\lambda$ and $a_2 < 3\lambda$, we obtain $N_{\rm TD} \le 2 \cdot 10^{17}$ cm^{-3} for large homogeneities and $N_{\rm TD} \ge 10^{19}$ cm^{-3} for small ones.

Conclusions

The investigation of the SALS dependence on the duration of the thermal treatment at 450 °C shows that the light scattering is connected to the nonhomogeneous distribution of TDs. Moreover, although the TD

A_1, cm^{-3}	A_2, s^{-1}	A_3, cm^{-3}	ρ_1, cm^{-3}	ρ_2, cm^{-3}
$5 \cdot 10^{13}$	0.17	$9 \cdot 10^{15}$	$2 \cdot 10^{6}$	10^{8}

concentration depends on the thermal treatment time linearly up to about 100 h, the SALS intensity is nonmonotonous in $t_{\rm tr}$. It stems from a wide range of spatial dimensions of micrononhomogeneities. The TD clusters with dimensions less than the light wavelength of the probing beam ($a < \lambda$) are formed on early stages of the thermal treatment. They are responsible both for the increasing of the SALS intensity and for its following decreasing when the proper concentration is attained. The clusters of the large size ($a > \lambda$) are generated at a lower rate and lead to a linear increasing of the SALS intensity. Thus, its dependence on the thermal treatment time becomes nonmonotonous.

One should take into account that here a model case is considered where the ensemble of clusters with the actual size distribution is approximated by clusters of two types with relevant averaged parameters. Therefore, one should be careful in respect to their parameter evaluation. Really, the analysis of the whole ensemble of clusters is needed, in accordance with Eq. (3). Moreover, for every type of clusters, the specific dependence of the local TD concentration on the thermal treatment time should be taken into account, e.g., as in Eq. (12). In this case, the larger the spatial size of the clusters, the longer the duration of the thermal treatment when this dependence remains linear. In principle, it would not deform the profile of the $I_d(t_{\rm tr})$ function but would essentially complicate the solution of the problem.

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Received 21.02.03.
Translated from Ukrainian by O.I.Voitenko

ДОСЛІДЖЕННЯ ПРОЦЕСІВ РОЗСІЮВАННЯ СВІТЛА В КРИСТАЛАХ КРЕМНІЮ З НЕОДНОРІДНИМ РОЗПОДІЛОМ ДОМІШОК

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Р е з ю м е

Проаналізовано причини немонотонної поведінки малокутового розсіювання світла (МКРС) в кристалах кремнію підчас переходу атомів домішки кисню в електрично активний стан в складі термодонорів (ТД). Показано, що безпосередньо причиною як зростання, так і зменшення МКРС в ході термообробки при 450 °С є утворення мікроскупчень ТД на місці вихідних мікрофлуктуацій концентрації кисню. З аналізу експериментальних даних отримано кількісні оцінки локальної концентрації ТД у мікроскупченнях різних розмірів.