The degree of polarization of Raman scattering of light in silicon nanocrystals

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Raman scattering of light (RS) on an array of oriented silicon nanocrystals was studied experimentally. The angular dependence of the intensity of the polarized components of the RS was measured and the parameter of the degree of polarization of scattered light was determined. It was found that the degree of polarization of the RS is related to the size of the nanocrystals in the samples. An array of nanocrystals with the same crystallographic orientation was obtained by thermal annealing of a silicon single crystal damaged by ion implantation. During thermal annealing of the sample, the crystallinity of the layer is restored not simultaneously in the entire damaged volume, but in the form of nanocrystals separated by amorphous area. All the clusters formed have the same crystallographic orientation of the original single crystal. The features of the degree of polarization of the RS in nanocrystals are associated with the quantum-mechanical uncertainty of the phonon wave vector and the uncertainty of the phonon direction in a limited volume of the nanocrystal. The relations linking the degree of polarization of the RS with the size of nanocrystals are obtained. A technique for determining the size of nanocrystals by measuring the degree of polarization of the RS is discussed.

Keywords: Raman scattering of light, silicon, nanocrystals, ion implantation, annealing, amorphous phase.

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1. Introduction

Creation of the crystal layers of silicon from the amorphous by the heat treatement methods is an important process task [1–3]. In particular, the pulse laser annealing technologies for the amorphous silicon can be applied to create crystal layers of silicon [1] and complex heterostructures with crystal inclusions of silicon with the crystal inclusions of silicon with sizes of several nanometers [2]. After the ion implantation, the thermal annealing of the defects and the amorphization of the crystal layer is a standard procedure of the microelectronics technology [4].

The application of the light Raman scattering spectroscopy (RS) allows determining conditions of occurrence of the crystalline phase on the amorphous layer, the sizes of separate crystallites, the volume portion of the newly-formed phase [1,2] and the portions of the oriented crystallites [3]. The study of the angular dependences of the intensity of the RS polarized components in these layers shows a significant portion of the ordered crystallites [1,3]. The studies of the newly-formed crystal layers produced by the advanced technologies of the pulse annealing or the simple thermal annealing have been performed to show that the crystal phase forms as appearing and growing clusters of the crystallite phase in the amorphous, while in the simple case of the thermal annealing the crystallite size is in a known way related to the annealing temperature [5,6].

The angular dependences of the intensity of the RS polarized components in the nanocrystals of the various size show the difference from the known dependences in the single crystal. These differences may be also related to some portion of the crystallites with the crystal-lattice orientation different from the main part [3]. The second reason of the difference is related to a specific feature of the Raman scattering on the small-sized nanocrystals [7]. Both the factors result in that the RS polarization degree of the nanocrystal will be different from the that value in the single crystal.

The presence of the sample with the fully oriented nanocrystals will allow specifically studying the impact of the nanocrystal size on the RS polarization degree. Such a sample was produced by using the sample of the single-crystal silicon with the (100) orientation, which was subjected to ion implantation of the carbon ions (C^+) with the dose of $5 \cdot 10^{16}\,cm^{-2}$ and the particle energy of 40 keV. After the implantation, the silicon layer becomes amorphous for the entire ion penetration depth. During the thermal annealing of the sample, the crystallinity of the layer is rebuilt as nanocrystals separated by amorphous gaps, and the formed nanocrystals have a predominantly crystal-lattice orientation of the initial single crystal.

The purpose of this study is to investigate the impact of the thermal annealing of implanted silicon layer on the RS polarization degree and to establish the usability of this dependence to determine the sizes of the newly-formed nanocrystals.

2. Uncertainty of the direction of the phonon wave vector in the nanocrystal and the RS intensity

In the *L*-sized nanocrystals, the quantum-mechanical uncertainty of the value of the wave vector of the optical phonon

$$\Delta q = 2\pi/L \quad (1)$$

turns out to be comparable with the value of the wave vector of the phonon **q** in the light scattering action. In the RS spectra of the nanocrystals, this manifests itself in the broadening of the spectrum line width Γ. The RS specific features in the silicon nanocrystals are studied in detail experimentally and theoretically in the studies [8–12], and it has established a relation of the shift and the width of the RS spectrum line to the size and the shape of the nanocrystal.

The uncertainty of the magnitude of the wave vector of the phonon (1) results in the uncertainty of the direction of the phonon **q** within the space of the reciprocal lattice. Thus, for the cubic lattice, the vector of the reciprocal lattice $G = 2\pi/a$ is determined by the lattice parameter a, and for the wave vector of the phonon in the small-sized crystal lattice (L) the discreteness of the directions is to be substantial:

$$\Delta\gamma = \frac{\Delta q}{G} = \frac{a}{L}. \quad (2)$$

In this case, instead of a definite direction of the wave vector of the phonon **q**, we can say about the direction towards some solid angle $\Delta\gamma$. The study [7] has demonstrated that in the geometry close to the back scattering the scattered light leaving the crystal will have a dispersion of the directions $\Delta\theta$:

$$\Delta\theta = \frac{nKa}{L}, \quad (3)$$

where n — the refraction index of the crystal, K — the constant of about 1. The direction dispersion angle can be measured in the experiment for measurement of the angular dependence.

Let us examine the light scattering in the laboratory coordinate system x, y, z in the back scattering geometry $y(zz)\bar{y}$ and $y(zx)\bar{y}$ as it is shown on Fig. 1.

The intensity of the scattered light is determined by the RS tensor **R** and the polarization direction of the incident and scattered light [13]:

$$I = A\sum_{\alpha}[e^i R(\alpha) e^s]^2. \quad (4)$$

The RS tensor for silicon in the main axes coinciding with the crystallographic directions of the lattice [100], [010], [001] has one independent magnitude d. Then the intensities of the polarized components of the scattered light

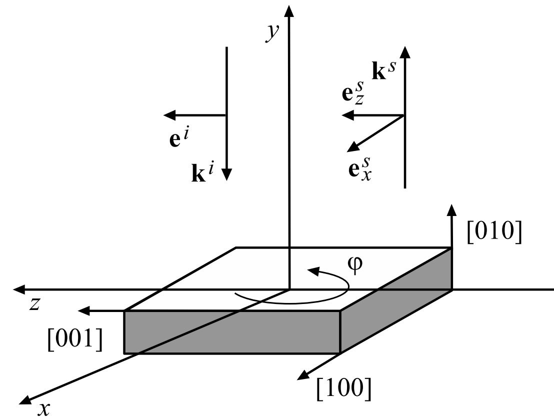

Figure 1. Scheme of RS measurement in the experiment: $\mathbf{k}^i, \mathbf{k}^s$ — the wave vectors of the incident and scattered light; $\mathbf{e}_i, \mathbf{e}_z^s, \mathbf{e}_x^s$ — the polarization vectors of the incident and scattered light.

along the k^s direction for the crystal rotated by an arbitrary angle φ:

$$I_{zx}(\varphi) = \frac{d^2}{2}[1 + \cos 4\varphi],$$
$$I_{zz}(\varphi) = \frac{d^2}{2}[1 - \cos 4\varphi]. \quad (5)$$

If there is the probability of scattering into some solid angle, as limited by the flat angle $\Delta\theta$, then along the direction k^s the photodetector will record the intensity averaged across this angle. By performing the calculations, we obtain the intensities for the two positions of the analyzer:

$$\overline{I_{zx}(\varphi)} = \frac{1}{\Delta\theta}\int_{-\Delta\theta/2}^{\Delta\theta/2} I_{zx}(\varphi+\theta)d\theta = \frac{d^2}{2}[(1 + \eta\cos 4\varphi)],$$

$$\overline{I_{zz}(\varphi)} = \frac{1}{\Delta\theta}\int_{-\Delta\theta/2}^{\Delta\theta/2} I_{zz}(\varphi+\theta)d\theta = \frac{d^2}{2}[(1 - \eta\cos 4\varphi)],$$

$$\eta = \frac{\sin(2\Delta\theta)}{2\Delta\theta}. \quad (6)$$

By turning the crystal in the experiment and measuring the intensities $I_x = \overline{I_{zx}(\varphi)}$ and $I_z = \overline{I_{zz}(\varphi)}$ — for the various angles φ, the formula (6) can calculate the magnitude η and determine the angle $\Delta\theta$.

The value η coincides with the determination of the radiation polarization degree for the sample oriented along the main axes. There are both the components in the total radiation: $I = I_x + I_z$. If orienting the crystal along the main axes $\varphi = 0$, then rotating the analyzer, the maximum intensity of the radiation coincides with $I_{\max} = I_x$, so does the minimum one with $I_{\min} = I_z$. Using the determination of the polarization degree from (6), we obtain

$$\frac{I_{\max} - I_{\min}}{I_{\min} + I_{\min}} = \eta. \quad (7)$$

This ratio can be used to find the parameter η and the angle $\Delta\theta$ by the two measurements of the intensity. If the orientation of the main axes of the crystal is not previously known, then the equation (6) shall be used.

3. Samples and measurement procedure

The single-crystal silicon (100) implanted with the carbon ions of the dose of $5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and the ion energy of $E = 40\,\mathrm{keV}$ becomes amorphous for the entire depth of the ion penetration. In the ion implantation, the amorphization of the single crystal is related to mixing of separate atoms of the crystal lattice, the formation of point defects and elastic distortions of the crystal lattice [4]. It turns out that the said dose is sufficient to manifest the silicon layer as the amorphous for the entire depth of light penetration in the optical measurements, which is confirmed by the measurements of the RS spectra (Fig. 2). The initial crystallinity of the layer is rebuilding during the thermal annealing of the sample. The crystallinity is rebuilding as separate regions separated by the amorphous gaps, and then, with the increase in the temperature, these regions are enlarging and merging to fill the entire volume of the layer, manifesting themselves in the RS spectra close to the oriented single crystal. Consequently, the formed nanocrystals have the crystal-lattice orientation of the initial single crystal.

The size of the nanocrystalline cluster in the amorphous matrix depends on the annealing temperature. The measurements of the sizes of the nanocrystals by the methods XRD [5] and the RS [6] have shown close values. The nanocrystals of the size 2 nm have appeared in the sample at the temperature of 700°C. At 800–900°C, the size increased to 6 nm, while at 1000°C it increased to 10 nm.

The plate of the implanted silicon was cut into several samples of the size 5×5 mm, which were annealed in a muffle oven at the temperatures 725, 770, 820, 870, 930, 970, 1100°C for 1 hour.The opposite side of the plate was used in the measurements as a reference single-crystal silicon.

The RS spectra of the samples were measured on the upgraded spectrometer DFS-52 with PMT H6240-01. The RS was induced by using the laser *LaserPhysics* 150t with the wavelength 488 nm and the power of 10 mW. The scattered light was recorded in the back scattering geometry $y(zz)\bar{y}$, $y(zx)\bar{y}$ and $y(z, z+x)\bar{y}$.

The monochromator's entrance slit width was 0.4 mm. The recorded spectra were analyzed using the software *Origin 8* for determination of the parameters of the spectrum line. The intensity of the spectrum line was determined as an area under the spectrum line of the crystallite phase approximated by the Voigt contour. The spectrum line width was determined as a Lorentz component of the Γ of the spectrum Voigt contour with the fixed Gaussian component Γ_g, equal to $3.1\,\mathrm{cm}^{-1}$, which is a tool spectrum width of the monochromator DFS-52 with the slit of 0.4 mm.

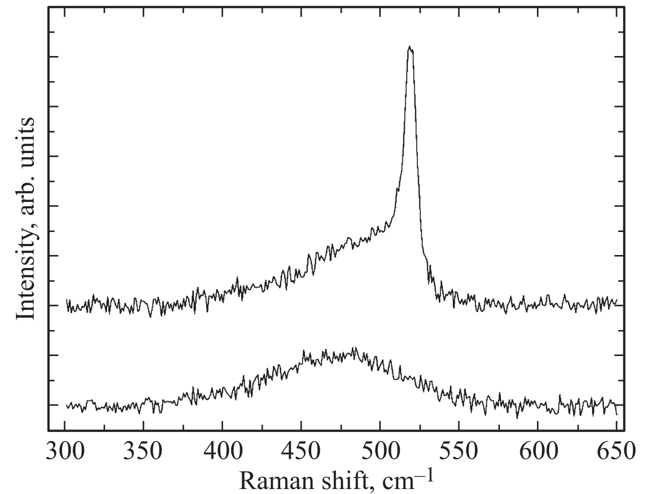

Figure 2. RS spectra of the experimental sample without annealing (the bottom curve) after the thermal annealing for 1 hour at 770°C (the top curve). The geometry of scattering $y(z, z+x)\bar{y}$.

The depth of collection of the scattered radiation l out of the sample in the absorption medium depends on the coefficient of light absorption α of the sample: $l \approx 1/2\alpha$. The depth of the amorphous layer of the ion-implanted samples with the energy of 40 keV is ~ 200 nm [4]. For the amorphous silicon, α depends on a technology of layer creation. For the hydrogenated amorphous silicon, for $\lambda = 488$ nm, $\alpha \approx 1.5 \cdot 10^5\,\mathrm{cm}^{-1}$ [14], the RS collection depth is ~ 30 nm. Using this evaluation, we obtain that penetration of the scattered light from beneath the amorphous layer was avoided in the experiment. All the recorded radiation was formed as a result of scattering of light by the amorphous phase, or by the nanocrystals generated during the thermal annealing of the amorphous silicon.

The experiment included the investigation of the radiation polarization degree and the measurement of the angular dependence of the RS radiation intensity. The studied sample was oriented along the crystallographic directions to have recorded the RS spectra of the sample in the geometries $y(zz)\bar{y}$, $y(zx)\bar{y}$ and $y(z, z+x)\bar{y}$, and then the sample was rotated around the axis y with a step 10° and the spectra were recorded in the geometries $y(zz)\bar{y}$, $y(zx)\bar{y}$ only. The spectrum in the geometry $y(z, z+x)\bar{y}$ was used to determine the radiation intensity I and the spectrum line width Γ, while the spectra in the geometries $y(zz)\bar{y}$, $y(zx)\bar{y}$ were used to determine the intensity of the respective polarized components I_x, I_z. The transmission coefficient of the polarizer $\boldsymbol{\tau} = I/(I_x + I_z)$ was monitored to be 0.71 ± 0.02.

4. Results and discussion

The RS spectrum of the sample without the annealing is a wide maximum within the range $480\,\mathrm{cm}^{-1}$ of the

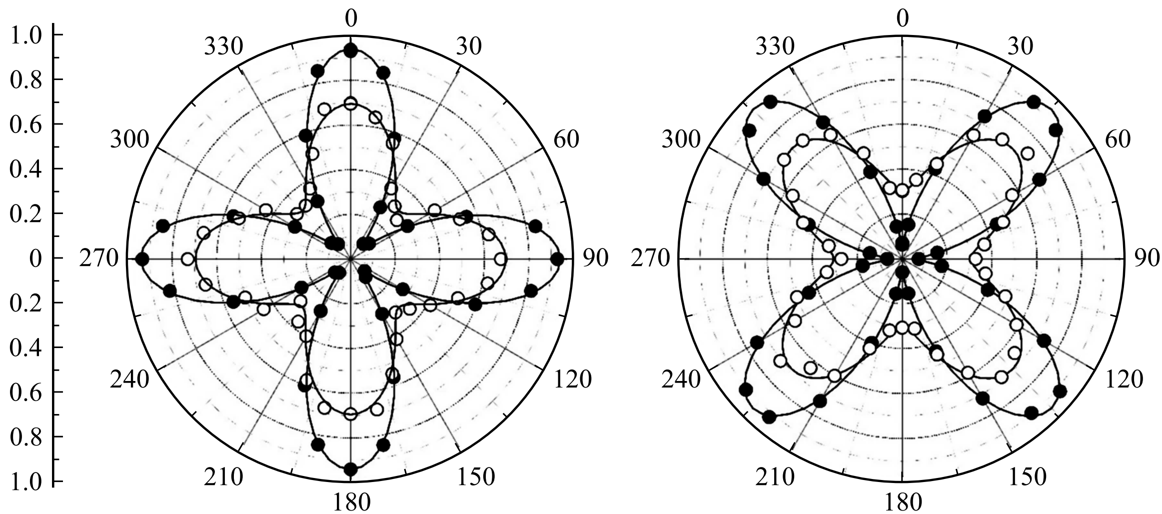

Figure 3. Angular dependences of the polarized RS components of the experimental samples I_x (on the left) and I_z (on the right). The silicon single crystal (the dark circles), the sample 770°C (the light circles). The solid line shows the results of fitting of the equation (6) by the least square method.

amorphous silicon, while the spectra of the samples after the annealing have the RS spectrum lines of the crystal phase of silicon $520\,\mathrm{cm}^{-1}$, as it is shown on Fig. 2.

The angular dependences of the intensity of the RS radiation of the polarized components I_x, I_z for the sample 770°C and the reference single crystal are shown on Fig. 3. The solid line of the figure shows the result of the fitting of the equation (6) by the least square method in order to determine the fitting parameter $\eta = 0.39$ for the sample 770°C and $\eta = 0.88$ for the single crystal. The angular dependences of the RS intensity for the samples produced at the temperatures 725, 820, 930, 970, 1100°C were not measured. The parameter η has been calculated by the formula (7) by the two measurements of the RS radiation intensity of the polarized components I_x, I_z.

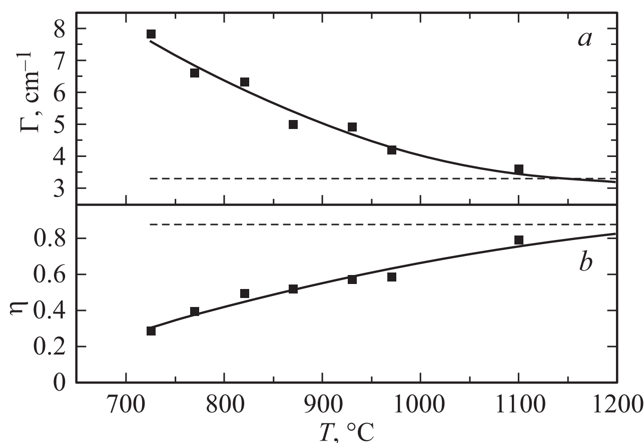

Figure 4. Dependence of the spectrum line width (a) and the RS polarization degree (b) of the silicon nanocrystals on the temperature of sample annealing. The dashed line shows the values for the single crystal.

Fig. 4 shows the results of the determination of the parameter η and the spectrum line of the crystal phase of the samples on the annealing temperature. The graph reflects the known result that the RS spectrum line width of the nanocrystals increases with the decrease in the size of the nanocrystal (with a lower temperature of annealing). The parameter η is proportional to the portion of the RS polarized radiation and the parameter value correlates to the spectrum line width and, consequently, the size of the nanocrystals in the samples.

It is necessary to ensure that the decrease in the RS radiation polarization degree of the nanocrystal array is not related to their disordering, the dispersion of the directions of their local crystallographic axes. It is, for example, due to the facts that the atoms of silicon were shifted from their points during the carbon ion implantation, and the thermal annealing did not fully return the lattice atoms to their point positions. Let us assume that the distribution of the dispersion is normal with the dispersion σ and the average value of the direction coincides with the crystallographic direction [100], then the portion of the crystals deflected by the angle θ will be:

$$P(\theta, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\theta^2}{2\sigma^2}\right).$$

By calculating the average intensity across the distribution, we obtain the intensities observed in the experiment:

$$I_x = \int_{-\pi}^{\pi} P(\theta, \sigma) I_{zx}(\varphi + \theta) d\theta = \frac{d^2}{2}\left[(1 + \mu \cos 4\varphi)\right],$$

$$I_z = \int_{-\pi}^{\pi} P(\theta, \sigma) I_{zz}(\varphi + \theta) d\theta = \frac{d^2}{2}\left[(1 - \mu \cos 4\varphi)\right],$$

$$\mu = \exp(-8\sigma^2). \tag{8}$$

Similar to the parameter η in (6), the parameter μ describes the decrease in the RS polarization degree, but by misorientation of the nanocrystal directions. The study [5] has shown that in implantation of C^+ with the said dose and energy, the mean square deviation of the lattice atoms is 0.02 nm. Let us assume that the formed nanocrystals keep their obtained inclination value, i.e. the orientation of the two nanocrystals of the size of 3 nm differs by the angles $\pm 0.02/3$. Assuming that this magnitude is equal to the square of the dispersion and using (8), we obtain $\mu = 0.95$. This value is much more bigger than the experimental value of the RS polarization degree. Consequently, the possible residual disordering of the nanocrystalline array can not be a reason of the reduction of the RS polarization degree η and a main reason of the reduction of the parameter η. But it is the uncertainty of the directions of the wave vector of the phonon in the nanocrystal.

The value η in the nanocrystals is determined by the angle $\Delta\theta$ for (6), which in turn is related to the size of the nanocrystallite from (3). The experimentally determined value η has a systematic error related to the imperfection of the polarizer and errors in the measurement of the angles. Thus, if reducing to an ideal case, where the single crystal has $\eta = 1$, then for the sample 770°C we obtain $\eta = 0.44$ and, by solving the equation $\sin(2\Delta\theta) = \eta 2\Delta\theta$, we obtain $\Delta\theta = 1.0$, i.e. the cone of uncertainty of the light scattering direction$\sim 60°$. Using (3), we obtain the evaluation of the size of the nanocrystal $L \approx 3$ nm for the sample 770°C. For the sample 1100°C $\eta = 0.89$, $\Delta\theta = 0.41$ and $L \approx 6$ nm.

In this case the calculations of the nanocrystal size as per (3) agree with the calculations for measurement of the spectrum line width [5]. It may be noted that the procedure for measuring the nanocrystal size based on the formula (3) is an analogue of the Scherrer formula for diffraction of the X-rays in the nanocrystals. The blurring of the diffraction peaks (widening) in the Scherrer formula is determined by the diffraction angle

$$\theta_d \cong \frac{\lambda}{L}.$$

The formula (2) has the same meaning, but for the optical phonons in the nanocrystal. The phonon quasi-pulse can always supplemented with the vector of the reciprocal lattice G, then the phonon wavelength in the Brillouin zone's center at $q \cong 0$ can be expressed through the vector of the reciprocal lattice:

$$\frac{2\pi}{\lambda_{\text{ph}}} = G \pm q \cong G.$$

Then the relationship (2) can be represented as follows

$$\Delta\gamma \cong \frac{\lambda_{\text{ph}}}{L}.$$

The observation of the decrease in the RS polarization degree in the nanocrystal can be related to the presence of a diffraction limit of the certainty of the direction of the optical phonons in the nanocrystal.

5. Conclusion

The experiment has investigated the RS on the array of the oriented nanocrystals of silicon of the various size. It has been found that the scattered light polarization degree is related to the size of the nanocrystals in the samples.

The calculations have been performed to show the relation of the RS polarization degree with the fundamental limit of the uncertainty of the direction of the wave vector of the optical phonon in the nanocrystals of the size of 2–10 nm. We have obtained the relationships to calculate the nanocrystal size by the measurements of the RS polarization degree.

The important part of the method of the determination of the nanocrystal size by the angular dependence of the RS intensity is that it is the polarized components of the intensity which are measured. As it is clear from (6), the total intensity of the two components does not depend on the angle of the crystal rotation. The equation (7) for determination of the polarization degree can be used only for the samples strictly oriented along the crystallographic directions.

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Conflict of interest

The author declares that he has no conflict of interest.

References

[1] D.V. Shuleiko, F.V. Kashaev, F.V. Potemkin, S.V. Zabotnov, A.V. Zoteev, D.E. Presnov, I.N. Parkhomenko, I.A. Romanov. Opt. Spectrosc., **124** (6), 770 (2018) (in Russian).
[2] A.V. Kolchin, D.V. Shuleiko, A.V. Pavlikov, S.V. Zabotnov, L.A. Golovan', D.E. Presnov, V.A. Volodin, G.K. Krivyakin, A.A. Popov, P.K. Kashkarov. Pis'ma ZhTF, **46** (11), 43 (2020) (in Russian).
[3] M.D. Efremov, V.V. Bolotov, V.A. Volodin, S.A. Kochubey, A.V. Kretinin. FTP, **36** (1), 109 (2002) (in Russian).
[4] V.S. Vavilov, A.R. Chelyadinskiy. UFN, **165** (3), 348 (1995) (in Russian).
[5] K.Kh. Nusupov, N.B. Beisenkhanov, S.K. Zharikov, I.K. Beisembetov, B.K. Kenzhaliev, T.K. Akhmetov, B.Zh. Seitov. FTT, **56** (11), 2231 (2014) (in Russian).
[6] A.V. Igo. Opt. i spektr., **129** (2), 1115 (2020) (in Russian).
[7] A.V. Igo. ZhETF, **158** (4), 605 (2020) (in Russian).
[8] H. Richter, Z.P. Wang, L. Ley. Solid State Commun., **39**, 625 (1981).
[9] I.H. Campbell, P.M. Fauchet. Solid State Commun., **58** (10), 739 (1986).
[10] V.S. Gorelik, A.V. Igo, S.N. Mikov. ZhETF, **109**, 2141 (1996) (in Russian).

[11] G. Faraci, S. Gibelisco, P. Russo, A.R. Pennisi, S.L. Rosa. Phys. Rev. B, **73**, 033307 (2006).
[12] V.A. Volodin, V.A. Sachkov. ZhETF, **143** (1), 100 (2013) (in Russian).
[13] M. Kardona, G. Gunterodt, R. Cheng, M. Long, G. Fogt. *Rasseyanie sveta v tverdykh telakh* (M., Mir, 1984) vyp. 2 (in Russian).
[14] M. Mulato, I. Chambouleyron, E.G. Birgin, J.M. Martínez. Appl. Phys. Lett., **77**, 2133 (2000).