CREATION OF DEFECTS IN Si CRYSTALS AFTER HIGH-ENERGY IRRADIATION BY ELECTRONS AND γ-QUANTA

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We studied the secondary processes in monocrystalline Si before and after both the irradiation by high-energy electrons (about 18 MeV) and the combined irradiation by electrons and γ-quanta by using X-ray diffraction analysis and the method of internal friction (IF) in the infrasound frequency range. It is shown that the irradiation influences the degree of structural perfection of crystals, deforms significantly the infrasound absorption spectrum, and induces the appearance of amplitude dependences and the temperature hysteresis of the effective modulus G_{eff}. Certain assumptions as for the nature of the phenomena observed are advanced.

Hard irradiation of semiconductor crystals leads to the appearance of radiation-induced defects (RD) in them [1—8]. The degree of radiation damage is defined by internal factors (the perfection of the initial crystal, content of admixtures, growing process, etc.), external factors (the energy and type of particles bombarding the material, the intensity and duration of irradiation, temperature, etc.), and the spatial distribution of created RD [7, 8]. The consideration of all these factors is a complicated task which has not been solved up to now. Primary RD generated under irradiation of Si are thermally unstable and rather movable. While migrating in a crystal, they can annihilate or create more stable complexes with one another and with the atoms of admixtures [2, 3]. As a result, the damage degree for an irradiated material is mainly defined by secondary processes which depend on a number of internal and external factors [5]. Due to the diversity of secondary processes, the contemporary state of theory does not allow one to infer on the nature of RD on the basis of calculations alone. Therefore, experiment plays the main role in solving this problem.

High brittleness of Si at low temperatures (of the order of room temperature) imposes some limitations on the possibility to use certain structure-sensitive methods (e.g., the static methods for studying elastic characteristics, which requires significant deformations). In this aspect, certain opportunities are provided by the method of IF which allows one to subtly investigate the mobility of dislocations and their interaction with various defects without any damage for a material under study at both low and high temperatures.

In the present work, we carried out the complex investigations of the structural perfection of monocrystals Si before and after the irradiation by high-energy (about 18 MeV) electrons and γ-quanta.

To attain our goal, we studied the profiles of spatial distribution of the intensity $I_h(x)$ of reflected X-rays and the low-frequency spectra of absorption of the elastic energy and the effective shear modulus G_{eff} in monocrystalline Si grown by the Czochralski method in direction $\langle 111 \rangle$.

We measured the elastic and inelastic characteristics of specimens of all groups by the method of reversible torsional pendulum in vacuum of about 10^3 Pa with a mean heating rate of 5-6 deg./min, which corresponds to the optimum rate of temperature changes. In this case, we can reveal the effects related to a change in the distribution of radiation-induced and intrinsic defects in Si [8]. The relative errors in the measurement of Q^{-1} and G_{eff} were, respectively, about 1 and 0.1%.

The modulus G_{eff} proportional to the square of the frequency of natural torsional oscillations of a specimen was measured simultaneously with the absorption of elastic energy at frequencies of about 2 Hz. Specimens for studying the elastic and inelastic characteristics were cut as parallelepipeds $1.5 \times 1.5 \times 80$ mm in the direction normal to the direction of growth so that the principal crystal axis was in plane (111).

The manufactured specimens were conditionally divided into four groups:

1) specimens of Si after a mechanical processing with diamond paste ACM-1/0 in the manufacture of "a Si

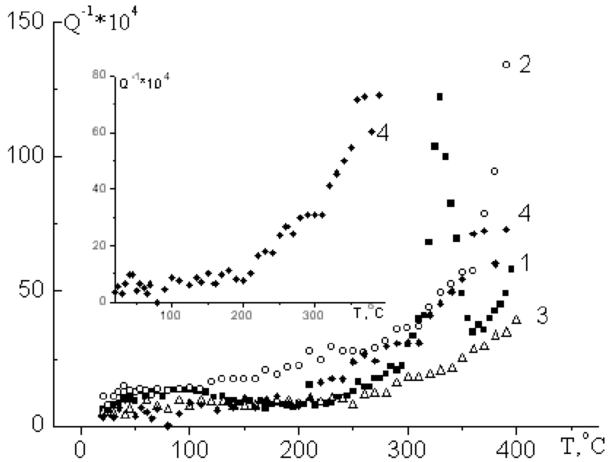

Fig. 1. Effect of irradiation on the temperature dependence of IF. The number of a curve coincides with that of a group

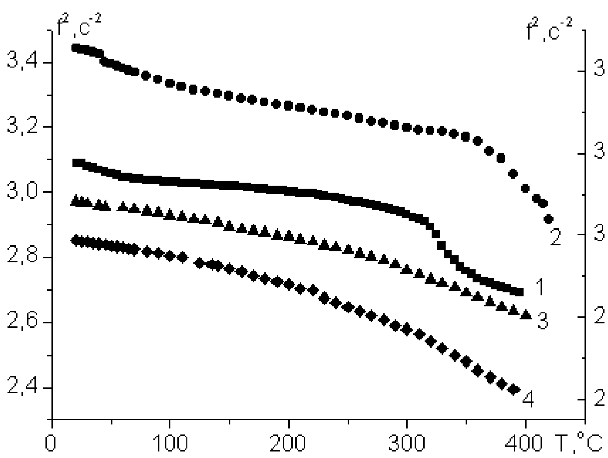

Fig. 2. Effect of irradiation on the temperature dependence of the effective shear modulus. The number of a curve coincides with that of a group

straw" (parallelepipeds 1.5 × 1.5 × 80 mm in size) and after the full cycle of chemical-mechanical processing under production conditions;

2) specimens irradiated by electrons with an energy of 18 MeV and a flux $\Phi_e = 1.8 \cdot 10^{13}$ electron/cm^2, which corresponds to the absorbed dose $D_e = 1.8$ kGy;

3) specimens irradiated by the double dose of electrons ($D_e = 3.6$ kGy) as compared with that for specimens of the second group;

4) specimens jointly irradiated by electrons ($D_\gamma = 3.6$ kGy) and γ-quanta ($D_\gamma = 4 \cdot 10^4$ rad).

To derive information as for the general state of a defect structure, the specimens were studied by the topographical Lang—Borman methods. On the topograms obtained, we observed both radial and longitudinal growth strips with a period of 150—200 mm.

We studied the profiles of distribution of the integral intensity $I_h(x)$ in the specimens by using a one-crystal spectrometer on symmetric reflexes (333), (555), and (777) in MoK_α emission. The variations in both the statistical Debye-Waller factor L and the coefficient of additional expenses of the energy of X-rays for diffusion scattering μ_d which characterize the structural perfection of a crystal on the whole [9] are calculated, and the radius R and the concentration n of possible microdefects are estimated. The results are presented in Table 1.

We note that, after the selective etching of the specimens of group 2, the growing dislocations with a density of $2.2 \cdot 10^3$ cm^{-2} were revealed. At the same time, the specimens of groups 3 and 4 showed the patterns of etching which are characteristic of microdefects. Their concentration was $2.4 \cdot 10^4$ cm^{-3}. Some of these patterns have significant size of 30 ÷ 40 mm. The comparison of the calculated values of R and n with those derived by the method of selective etching confirm the validity of the estimates and the correctness of the choice of a method for calculations.

The results of studies of the temperature dependences of IF and G_{eff} for specimens of all the groups are given in Figs.1 and 2. The spectrum of absorption of the elastic energy versus temperature for the specimens of group 1 (Fig. 1, curve *1*) includes a number of weakly differentiated maxima in the interval 20—150 °C and a complicated maximum at 290—330 °C which correspond to the characteristic changes in G_{eff} with temperature (Fig. 2, curve *1*, Table 2). The behavior of $G_{\text{eff}}(T)$ supports the assumption on the relaxation nature of the majority of observed maxima except for the peaks at 70 and 330 °C. For example, the latter corresponds to a decrease in the diminution rate of G_{eff} ($\partial G_{\text{eff}}/\partial T$) with temperature, which supports the assumption on its hysteresis character [7]. Moreover, this maximum is deformed at cooling in such a way that it becomes clear that the adsorption of elastic energy is governed by at least two different mechanisms. It is

T a b l e. 1. Radius R and the concentration n of defects for specimens of groups 2 and 3

Number of group	(hkl)	R_{calc}, mm	R_{exp}, mm	n_{calc}, cm^{-3}	n_{exp}, cm^{-3}
2	333	29	23	$3.6 \cdot 10^3$	$7.1 \cdot 10^3$
	555	9	9	$9.7 \cdot 10^5$	$1.1 \cdot 10^5$
3	333	10	10	$5.4 \cdot 10^4$	$3.7 \cdot 10^4$
	555	–	6		$3.0 \cdot 10^5$
	777	12	4	$3.0 \cdot 10^4$	$2.3 \cdot 10^8$

worth noting that the temperature hysteresis of the shear modulus for this group of specimens is observed only in the temperature region where maxima are observed, which also confirms our assumption on their nonrelaxation character. It is clear that such effects can be related to essential structural transformations occurring in Si at heating and cooling in these temperature intervals.

The results of studying the temperature dependences of both the adsorption of elastic energy and the effective shear modulus for the specimens of group 2 are given by curves *2* in the same figures. Irradiation leads to the significant deformation of their adsorption spectrum, namely, the adsorption background in the region 100—300 °C is significantly enhanced and the complicated effect in the region 280—330 °C is smoothed away. In this case, we revealed the remarkable nonstability of the temperature dependence of $G_{\rm eff}$ and a significant hysteresis of the curves of $G_{\rm eff}(T)$ under heating and cooling. This indicates the increase in both the total number of defects participating in the process of adsorption and the mobility of the dislocation-admixture structure or, more exactly, the increase in the concentration of dislocation loops and the enhancement of their role in the adsorption of elastic energy.

The doubling of irradiation dose leads to a decrease of the adsorption background practically by two times in the interval of 20—250 °C, a further damping of the maxima at 300—350 °C, and a clearer differentiation of the peaks at 20—260 °C on the curves $Q^{-1}(T)$ (Fig. 1, curve *3*). We emphasize the appearance of sections on the IF curves which are accompanied by a relative increase in the effective shear modulus $G_{\rm eff}(T)$ under the increase in temperature from 50 to 150 °C.

The combined irradiation of the specimens of group 4 led to some renewal of the effect near 330 °C, the increase in adsorption in the interval 20—50 °C by a factor 1.8 as compared to the specimens of group 3, and the appearance of a maximum at 430 °C (Fig. 1, the insert).

T a b l e. 2. Parameters of relaxation effects for the specimens of group 1

Number	$T_{\max}$, °C	$Q^{-1}\cdot 10^4$	$E_{\max}$, eV
1	40	3	0.72
2	50	3	0.74
3	63	4	0.77
4	79	6.5	0.81
5	104	5.5	0.87
6	278	6	1.3
7	335	58	1.45

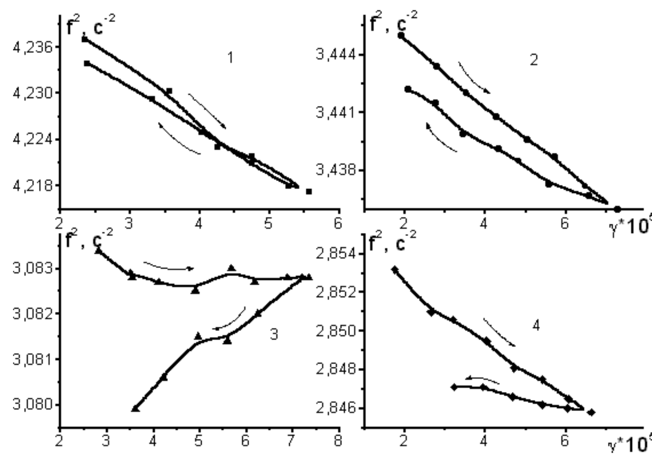

Fig. 3. Effect of irradiation on the amplitude dependence of the effective shear modulus. The number of a curve coincides with that of a group

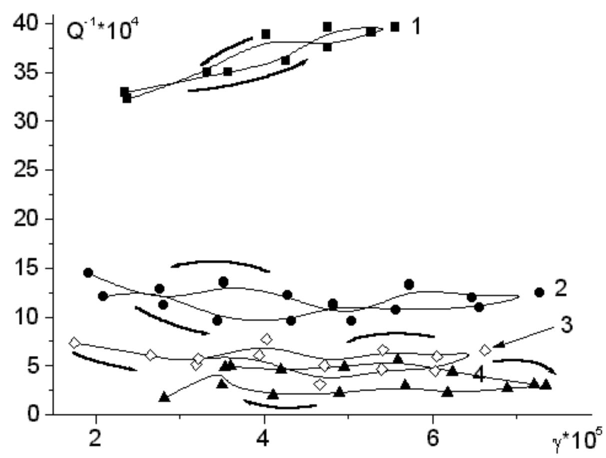

Fig. 4. Effect of irradiation on the amplitude dependence of IF. The number of a curve coincides with that of a group

The dynamical annealing of the specimens of group 2 which was carried out in the mode of thermocycling in the interval 20—400 °C led to the higher differentiation of low-temperature maxima and the partial renewal of the effect at 330 °C. In this case, the remarkable nonlinearities on the temperature dependences of $G_{\rm eff}$ were smoothed, i.e., the formation of the adsorption spectrum was accompanied by the stabilization of $G_{\rm eff}(T)$, which can be a result of the significant stabilization of the imperfect structure. We may assume that there occurs the compensation of the contributions of micro- and macrodeformations, but the influence of dislocation loops on IF remains rather weighty even after 6—8 such cycles. This is supported, in particular, by the amplitude dependences of IF and $G_{\rm eff}$ in Figs. 3 and 4. As seen, the appearance of the amplitude dependence of $G_{\rm eff}$ and the open character of curves of $G_{\rm eff}(\gamma)$ under increase and decrease of the relative deformation amplitude γ indicate the presence of complicated secondary processes in irradiated specimens. This can be a result of the facilitated separation of dislocation folds from point-like defects fixing them or the appearance of dislocation sections which are free from admixtures. An increase in the irradiation dose increases significantly the concentration of fixing centers, which leads, in turn, to a decrease in $\Delta f^2/\Delta\gamma$ from $5.3 \cdot 10^{-3}$ to $1.1 \cdot 10^{-3}$. That is, there occurs a decrease in the amplitude dependences of the effective modulus (the fixing of dislocation folds of RD). However, this is accompanied by the remarkable nonclosedness of the curves of $G_{\rm eff}(\gamma)$ upon the increase or decrease in the relative deformation γ (Fig. 4) which strengthens with increase in the dose of electron irradiation. The combined irradiation led to some weakening of the above-mentioned effect. Such a behavior of $G_{\rm eff}(\gamma)$ in irradiated specimens can be explained by the increase in the mobility of dislocation folds, which is improbable at the great amount of RD in the irradiated crystal, or by the appearance of free dislocation loops. Indeed, the results of structural studies confirm the presence of microdefects with large size in irradiated Si, which is equivalent to the appearance of dislocation loops in the structure whose concentration is proportional to that of observed microdefects. This increase in the density of dislocation loops in the crystal which are free from admixtures and RD influenced the behavior of IF and $G_{\rm eff}$ under conditions of a change in γ. Therefore, the curves of the amplitude dependences of $G_{\rm eff}$ become open with increase or decrease in γ. Moreover, the anomalous behavior of Q^{-1} with a change in the deformation indicates that they are just the dislocation loops rather than ordinary linear dislocations (Fig. 4).

The analysis of the temperature behavior of the IF spectra and the X-ray structural analysis of the irradiated specimens allow us to advance some assumptions about the possible nature of the observed phenomena. It is most probable that at least two types of microdefects are formed in Si irradiated by high-energy electrons: small and larger microdefects up to 10 and 30—40 mm in size, respectively. Our studies allow us to assume also that the first type is the vacancy complexes (VV-complexes), because the maxima in the spectra of irradiated Si (contrary to the control specimens of group 1) in the region 180—220 °C appeared and were strengthened under dynamical thermocycling. Such defects are characteristic of just VV-accumulations in plane (111) of Si [10]. As known, vacancy complexes are more advantageous in energy than single vacancies in Si. Therefore, the former will be observed in this material after its saturation by vacancies from the surface due to its mechanical processing (see [10]) or at the expense of the irradiation by high-energy particles. We note that the above-mentioned complexes are evidently formed already in the process of irradiation or at once after it, because the X-ray diffraction studies are carried out with irradiated specimens which do not undergo any thermal treatment for some time except for the natural aging at $T_{\rm room}$. Such an assumption well correlates with the temperature dependence of the IF spectra of irradiated specimens and allows one to explain the appearance of the hysteresis of curves and the significant weakening of the effect in the region 280—330 °C after the irradiation by electrons. The nature of the above-mentioned maximum is related to the initial stages of evolution of oxygen from the supersaturated solid solution at 400 °C [11]. Indeed, the investigation of the nature of these maxima carried out by us shows that their height and temperature position are defined by the annealing duration at 400 °C and well correlate with the concentration of thermodonors of the 1st type of several different kinds (TD_{1A}, TD_{1B}, TD_{1C}, etc.). According to the modern ideas, the process of creation of TD_1 in Si is defined by the concentration of moving structural units (MSU) which supply oxygen to separations SiO_x. Therefore, the binding of vacancies which could enter the composition of MSU should decelerate the process of aging and lead to a significant decrease in the adsorption related to this process, which is observed in experiments. Some renewal of the maximum near 330 °C after the additional irradiation by γ-quanta indicates, possibly, that this type of irradiation does not promote the formation of VV-complexes. However, to confirm the above-mentioned reasoning, some additional studies are needed.

Thus, we have established and investigated the low-frequency temperature and amplitude spectra of adsorption of the elastic energy and the effective shear modulus $G_{\rm eff}$ in monocrystalline Si irradiated by various doses of electrons and γ-quanta. We have shown also that the irradiation by high-energy electrons (about 18 MeV) gives rise to the appearance of a significant amount of microdefects and dislocation loops of remarkable size (30—40 mm) in the structure of Si which change essentially both mechanical and X-ray diffraction spectra and advance certain assumptions about the possible nature of the observed phenomena.

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ДЕФЕКТОУТВОРЕННЯ В КРИСТАЛАХ КРЕМНІЮ ПІСЛЯ ВИСОКОЕНЕРГЕТИЧНОГО ЕЛЕКТРОННОГО І γ-ОПРОМІНЕННЯ

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Р е з ю м е

Проведено рентгеноструктурні дослідження та дослідження методом внутрішнього тертя (ВТ) в інфразвуковій області частот вторинних процесів у монокристалічному кремнії до і після опромінення електронами високих (близько 18 МеВ) енергій та комбінованого опромінення електронами і γ-квантами. Показано, що опромінення впливає на ступінь структурної досконалості кристалів, значно деформує спектр поглинання інфразвуку та приводить до появи амплітудних залежностей і температурного гістерезису ефективного модуля $G_{\text{еф}}$. Зроблені припущення щодо природи спостережуваних явищ.

ДЕФЕКТООБРАЗОВАНИЕ В КРИСТАЛАХ КРЕМНИЯ ПОСЛЕ ВЫСОКОЭНЕРГЕТИЧЕСКОГО ЭЛЕКТРОННОГО И γ-ОБЛУЧЕНИЯ

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Р е з ю м е

Проведены рентгеноструктурные исследования и исследования методом внутреннего трения в инфразвуковой области частот релаксационных процессов в монокристаллическом кремнии до и после облучения электронами высоких (приблизительно 18 МэВ) энергий и комбинированного облучения электронами и γ-квантами. Показано, что доза облучения влияет на степень структурного совершенства кристаллов, значительно деформирует спектр поглощения инфразвука и приводит к появлению амплитудных зависимостей и температурного гистерезиса $G_{\text{эф}}$. Сделаны предположения относительно природы наблюдаемых явлений.