ON THE NATURE OF "NEGATIVE" ANNEALING OF THE NONEQUILIBRIUM CHARGE CARRIER LIFETIME IN IRRADIATED n-Si

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UDC 621.315.592
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A variation of the recombination properties of pre-irradiated (by gamma quanta of ^{60}Co at 30 °C) Czochralski n-silicon during annealing at 20—350 °C as well as during the 1-MeV electron irradiation at the same temperature range of has been studied. The reduction of the lifetime τ of nonequilibrium charge carriers (NCCs) after annealing in the temperature range 200—300 °C ("negative" annealing) was found to be caused by the formation of V_2O complexes ($V_2 + O \rightarrow V_2O$), in particular, because the hole capture cross-section of those complexes is larger than that of V_2 defects. It has been found that the formation and annealing of V_2O complexes are characterized by the activation energies 1.35 and 1.6 eV, respectively, while the hole capture cross-section of those defects is $\sigma_p = 3 \times 10^{-13}$ cm^{-2}.

1. Introduction

High-energy irradiation of semiconductor crystals leads to the reduction of the lifetime of NCCs, owing to the formation of extra recombination centers. As a rule, after the irradiated samples having been annealed, irradiation-induced defects (IIDs) disappear, and the lifetime recovers, partially or completely, to its initial value. However, in Cz n-Si irradiated at room temperature either with γ-quanta from a ^{60}Co source or with 1-MeV electrons, a reverse effect is observed. It means that, if the samples are annealed isochronously within the temperature range 180—300 °C, the NCCs' lifetime τ becomes shorter.

This effect, the so-called "negative" annealing of τ, has been observed for a long time (see, e.g., works [1–5]). Nevertheless, such a behavior of τ has no unequivocal explanation till now, although it can be of practical interest from the viewpoint of the radiation technology for controlling the properties of silicon-based devices. The analysis of the available body of researches concerning this problem allowed us to distinguish between the following basic interpretations of the phenomenon:

— In works [1, 2], the "negative" annealing of τ was associated with the annealing of VO-centers.

— In work [3], on the basis of a comparison between the data concerning the annealing of τ and the recombination emission spectra, a supposition was made that the "negative" annealing of τ is caused by the generation of new defects, which are responsible for band C. Those defects may probably contain oxygen, have a level at $E_c - 0.36$ eV, and are formed at such temperatures, when A-centers are still not annealed out.

— In works [4, 5], the "negative" annealing of τ was associated with the formation of extra defects in the course of annealing with a deep acceptor level at $E_c - (0.45 \pm 0.02)$ eV. Those complexes were supposed to be C_iO_i—V_2.

This work aimed at obtaining the new information concerning the origin and recombination characteristics of IIDs, which govern the "negative" annealing of τ in irradiated n-Si.

2. Experimental Part

In our researches, we used Cz n-Si samples with the concentration $n_0 = 1 \times 10^{15}$ cm^{-3} and the initial lifetime $\tau_0 = 100 \div 130$ μs of free electrons (KEF-4.5), and with $n_0 = 2.5 \times 10^{13}$ cm^{-3} and $\tau_0 = 40 \div 50$ μs

(designated as KEF-200); the concentration of oxygen was $N_O = (6 \div 7) \times 10^{17}$ cm^{-3}, and the concentration of carbon was $N_C \leq 5 \times 10^{16}$ cm^{-3}. The samples had the form of a $10 \times 4 \times 2.5$-mm^3 rectangular bar.

The samples were irradiated with either γ-quanta from a ^{60}Co source (with the radiation intensity $J_\gamma = 2 \times 10^{11}$ quantum/(cm^2 $\times$ s), to the exposure dose $\Phi = 4.16 \times 10^{15}$ cm^{-2}, and at a temperature $T_{\rm irr} = 30$ °C) or 1-MeV electrons (with the electron beam intensity $J_e = 3 \times 10^{11}$ electron/(cm$^2 \times$s), to the dose $\Phi = 1 \times 10^{13}$ cm^{-2}, and at a temperature $T_{\rm irr} = 20$ °C).

The NCC lifetime τ was determined at room temperature by the relaxation of nonequilibrium photoconductance and provided a low level of excitation, i.e. we determined the value of τ for holes, minority charge carriers in n-Si. The estimation error for τ did not exceed 10%.

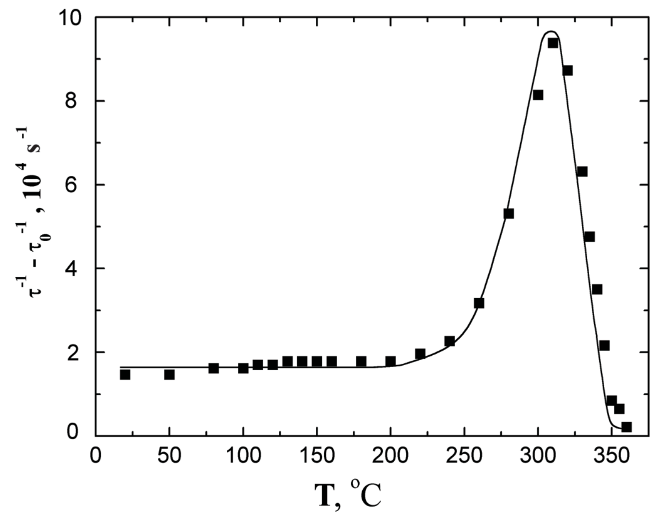

Fig. 1. Experimental (points) and calculated (solid curve) dependences of the quantity Δ $(1/\tau)$ on the temperature of isochronous (10 min) annealing $T_{\rm ann}$ of KEF-200 samples irradiated with γ-quanta

3. Results and Their Discussion

In Fig. 1, experimental points correspond to the dependence of the quantity $\Delta(1/\tau) = 1/\tau - 1/\tau_0$ on the temperature of isochronous (for 10 min) annealing $T_{\rm ann}$ for γ-irradiated KEF-200 samples; here, τ is the NCC lifetime measured after every step of annealing. The samples were annealed in the temperature range $T_{\rm ann} = 20 \div 360$ °C by a step of 5—30 °C. The figure demonstrates that $\Delta(1/\tau)$ grows in the temperature range from 200 to 300 °C, decreases in the interval from 300 to 360 °C, and, at 360 °C, recovers to approximately 90% of the initial value τ_0. That is, there is a peak of the “negative” annealing of τ in the dependence $\Delta(T)$. The “negative” annealing of τ evidences for the formation of either extra dominant centers of recombination or IIDs, which are recombinationally more active than those introduced after irradiation. The temperature interval of 200–300 °C is an interval, where divacancies (V_2) in Cz n-Si become annealed out [6–11]. Annealing of V_2 can proceed through a decay of divacancies followed by the formation of VO-centers, which are the dominating centers of recombination in the irradiated Cz n-Si [12], or by the migration of V_2 as whole entities and the formation of V_2O-complexes, which, in their turn, are annealed in the temperature range from 300 to 350 °C [7, 10, 13]. The VO-centers are annealed in the same temperature interval [14].

In order to elucidate which defects — VO or V_2O — are responsible for the “negative” annealing of τ, we carried out an experiment consisting in the irradiation of thick KEF-4.5 samples by electrons with an energy of about 1 MeV at high temperatures (from 20 to 350 °C). By convention, the samples, whose thickness exceeded the thickness of the layer that ensured the complete absorption of 1-MeV electrons, were regarded as “thick”. The irradiation of the samples at the IID annealing temperatures enabled the direct monitoring over the transformation of IIDs. At the same time, the use of “thick” samples and the application of techniques developed for near-surface researches allowed us to split the contributions of the primary IIDs of the vacancy and divacancy types.

Every specimen was e-irradiated from the side of one of its largest facets, while τ was measured on the both. The thickness of the sample should be chosen such that makes the electron energy on the shadow side of the sample lower than or close to the threshold energy of divacancy formation. In this case, if “negative” annealing was caused by the IIDs of the divacancy origin, it would be absent at the shadow side of the sample. Let us estimate the sample thickness which is necessary for such an experiment.

The energy spectrum of an electron beam produced by an Argus linear accelerator of electrons, which was used in our experiments, extended over 0.3—1.4 MeV and peaked at 1 MeV; about two thirds of electrons had the energy of (1 ± 0.2) MeV. The main energy losses of such electrons are spent for ionization [15]. For 1-MeV electrons, the ionization energy losses in Si amount to approximately 360 keV/mm.

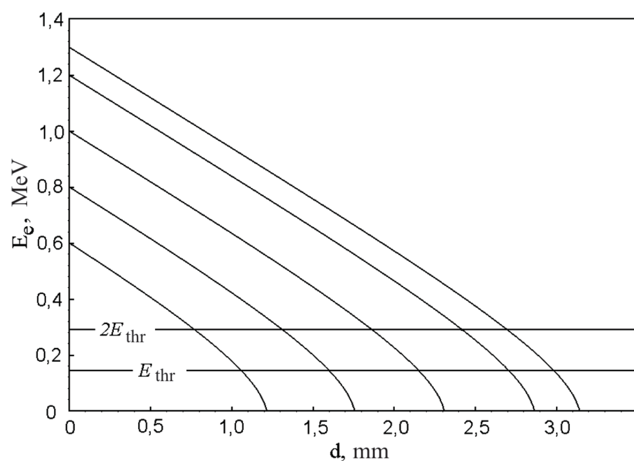

Fig. 2. Variation of the electron energy as a function of the electron penetration depth into a silicon sample for various initial electron energies: 0.6, 0.8, 1, 1.2, and 1.3 MeV (from bottom to top)

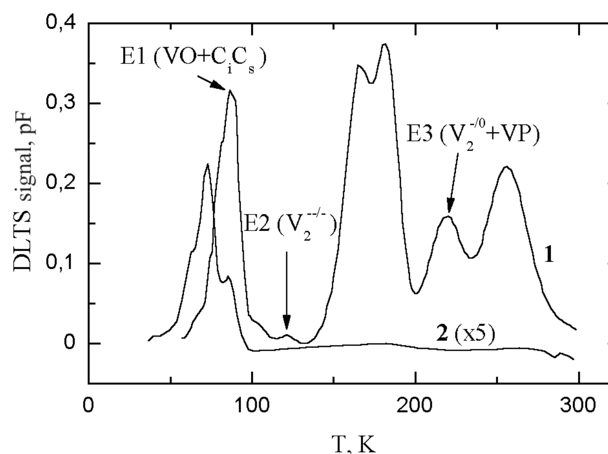

Fig. 3. DLTS spectra measured on the e-irradiated (*1*) and shadow (*2*) sides of a KEF-2 sample at room temperature [17]. The relevant parameters are: the electron energy is 1 MeV, $n_0 = 2 \times 10^{15}$ cm^{-3}, $N_{\rm O} = 6 \times 10^{17}$ cm^{-3}, $N_{\rm C} < 1 \times 10^{17}$ cm^{-3}, and $\Phi = 4 \times 10^{15}$ cm^{-2}

Figure 2 demonstrates how the electron energy varies depending on the electron penetration depth into a silicon sample. The calculations were carried out, making use of formula (86) in work [15], for electrons with various initial energies. The horizontal line $E_{\rm thr} \approx$ 145 keV marks the threshold energy for electrons in Si [16]. It is the minimal energy value that is necessary for electrons to form a Frenkel pair. If the electron energy exceeds $2E_{\rm thr}$, the displacement of two neighbor atoms becomes possible, so that complexes V_2 may be formed. It is evident from the figure that, in the case of our energy spectrum of electrons, the formation of V_2-complexes in the near-surface layer on the shadow side of the sample is improbable for the sample's thickness of about (2.5 ± 0.2) mm, whereas the formation of Frenkel pairs has to occur. It is confirmed by the deep-level transient spectroscopy (DLTS) measurements carried out at both sides (irradiated by electrons at room temperature and shadow ones) of a KEF-2 sample 2.35 mm in thickness, the results of which are given in Fig. 3 [17]. The comparison of the spectra makes it evident that peaks E_2 and E_3, which are related to the divalent $V_2^{--/-}$ (E_c − 0.23 eV) and monovalent $V_2^{-/0}$ (E_c − 0.42 eV) acceptor states of divacancies, respectively, can be observed only on the irradiated side of the sample. At the same time, the peak related to VO-centers (E_1, $E_c-0.17$ eV) is present in both spectra, with the efficiency of the formation of VO-centers on the shadow side being approximately an order of magnitude lower than that on the irradiated one.

While measuring τ, an AL-107 GaAs-based light-emitting diode with a wavelength of 0.96 μm was used to ionize the crystal. Such light is absorbed within the near-surface layer of Si about 50 μm in thickness. The thickness of the NCC recombination region can be determined by evaluating the diffusion length of holes

$$l_p = \sqrt{D_p \tau}, \qquad (1)$$

where D_p is the hole diffusion coefficient. For the KEF-4.5 samples, the initial lifetime $\tau_0 = 100 \div 130$ μs. Using Eq. (1), we obtain that the complete recombination takes place within a near-surface layer not thicker than 0.40—0.45 mm. After irradiating the sample at various temperatures, τ becomes about $10 \div 20\,\mu$s on the irradiated side (accordingly, the recombination region thickness is about 0.15—0.20 mm), and about 70 μs on the shadow one (the recombination region thickness is about 0.30 mm). Therefore, our estimations and our researches testify that the thickness of 2.5 mm is close to optimal for KEF-4.5 samples under the conditions of our experiment.

In Fig. 4, the dependences of the quantity $\Delta = 1/\tau_e - 1/\tau_0$, where τ_e is the NCC lifetime after the e-irradiation, on the irradiation temperature $T_{\rm irr}$ are shown within the range from 20 to 350 °C for the irradiated and shadow sides of KEF-4.5 specimens. At every temperature within the indicated interval, each individual sample was subjected to e-irradiation to the same exposure dose $\Phi = 1 \times 10^{13}$ cm^{-2}. One can see from the figure that the values of Δ almost do not change in

the range $T_{\rm irr} = 20 \div 300$ °C, being approximately an order of magnitude smaller on the shadow side of the sample. In the temperature range $T_{\rm irr} = 300 \div 350$ °C, where VO-centers are annealed, the value of Δ on the shadow side decreases. The dependence of $\Delta(T_{\rm irr})$ for the irradiated side looks, by its shape and the temperature arrangement, like the dependence $\Delta(T_{\rm ann})$ for the KEF-200 sample exhibited in Fig. 1. Hence, if the samples are irradiated with electrons in the range of annealing temperatures for V_2($T_{\rm irr} = 200 \div 300$ °C), the value of Δ drastically increases on the irradiated side and does not change on the shadow one. In the near-surface layer on the irradiated side, in contrast to the shadow one, there are V_2. It may mean that the increase of Δ in the temperature range of 200—300 °C both on the *e*-irradiated side of KEF-4.5 samples (Fig. 4) and for γ-irradiated KEF-200 samples (Fig. 1) was caused by the annealing of V_2.

Those IIDs of the divacancy origin are, most possibly, V_2O-complexes. At the same time, the formation of C_iO_i-V_2-complexes, which was supposed in works [4, 5], is hardly probable, because the concentration of C_iO_i-complexes (as well as the concentration of all IIDs altogether), which are formed in the course of the irradiation of the samples to our exposure doses, is much more lower – by almost six orders of magnitude — than the concentration of O_i. In works [7–11], where the DLTS was used to study the electric properties of V_2O, it was shown that V_2O- and V_2-complexes are divalent acceptors in Cz *n*-Si which have almost identical energies of recharge activation: about 0.23 eV for $V_2O^{--/-}$ and $V_2^{--/-}$, about 0.47 eV for $V_2O^{-/0}$, and 0.42 eV for $V_2^{-/0}$. The effective cross-sections of electron capture for $V_2O^{--/-}$ and $V_2^{--/-}$ are approximately equal to each other. At the same time, the electron capture cross-section for $V_2O^{-/0}$ is almost an order of magnitude larger than that for $V_2^{-/0}$. This means that $V_2O^{-/0}$ can be a more effective center of recombination than $V_2^{-/0}$.

Now, let us analyze our experimental data quantitatively. From the viewpoint of our previous considerations, the peak of the "negative" annealing of τ in the experimental dependence $\Delta(T_{\rm ann})$ for γ-irradiated KEF-200 samples (Fig. 1) was caused by the formation (at 200—300 °C) and annealing (at 300—350 °C) of V_2O-complexes. The corresponding kinetic equation that describes those processes looks like

$$\frac{dN_{V_2O}}{dt} = \chi_{V_2O}N_{V_2}N_{O} - k_{V_2O}N_{V_2O}, \tag{2}$$

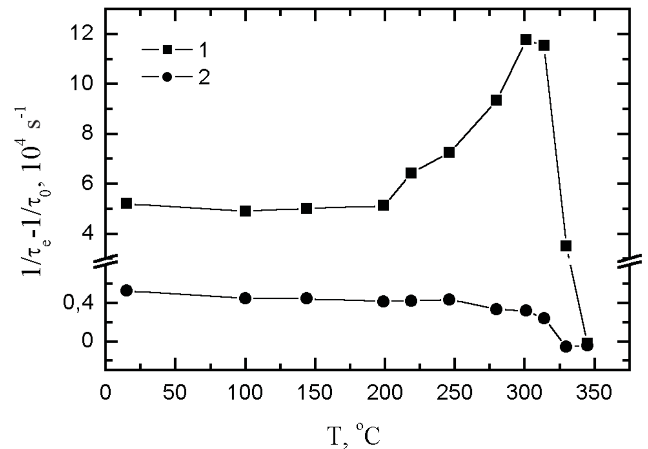

Fig. 4. Dependences of the quantity $\Delta(1/\tau)$ on the irradiation temperature $T_{\rm irr}$, measured on the *e*-irradiated (*1*) and shadow (*2*) sides of KEF-4.5 samples

where N_{V_2O} is the concentration of V_2O-complexes, χ_{V_2O} is the constant of V_2 capture by oxygen atoms,

$$k_{V_2O} = \nu \exp\left(-\frac{E_a}{kT}\right), \tag{3}$$

and ν and E_a are the frequency factor and the activation energy of V_2O-complex annealing, respectively.

Expressions (2) and (3) were used to describe the results of the experiment exhibited in Fig. 1. The solid curve in this figure represents the results of our calculation in the case where the formation of V_2O-complexes is characterized by the parameters E_a = 1.35 eV and $\nu = 3.3 \times 10^8$ s^{-1}, their annealing by the parameters $E_a = 1.56$ eV and $\nu = 2.5 \times 10^{10}$ s^{-1}, and the cross-section of hole capture by these complexes is equal to $\sigma_p = 3 \times 10^{-13}$ cm^{-2}. The values were obtained by the computer-assisted fitting of the theoretical results to the experimental ones. Our results concerning the formation of V_2O-complexes agree well with the data of work [11], where it was found experimentally that the annealing of V_2-defects and the formation of V_2O-complexes are characterized by the same activation energy of about 1.3 eV. This is an additional argument in favor of that the "negative" annealing of τ is caused by the formation of V_2O-complexes.

In the material of the studied KEF-200 samples, the Fermi level is located at $Ec - 0.36$ eV. This means that only the monovalent states of V_2 and V_2O manifest their recombination activity. Therefore, the value $\sigma_p = 3 \times 10^{-13}$ cm^{-2} obtained by us concerns $V_2O^{-/0}$. It is almost the same as that for VO-centers [12] and much larger than $\sigma_p = 3 \times 10^{-15}$ cm^{-2} for

$V_2^{-/0}$ [18], so that divacancies contribute insignificantly to the recombination. At γ-irradiation, the efficiency of the formation of primary V_2 (and, hence, the maximal concentration of V_2O) is approximately two orders of magnitude smaller than that of VO-centers [12]. Nevertheless, at room temperature, the electron population of VO-centers is three orders of magnitude lower than that of $V_2O^{-/0}$-ones owing to a deeper location of the level in the forbidden gap of Si. Therefore, it is $V_2O^{-/0}$ that govern the recombination of NCCs.

4. Conclusions

Thus, the variation of the recombination properties of e- or γ-irradiated Cz n-Si, when it is annealed in the temperature range $T_{\rm ann} = 200 \div 350$ °C, is governed by the processes of the annealing of V_2, through the diffusion of the latter, which results in the formation and the subsequent annealing of V_2O-complexes. The formation of V_2O-complexes brings about a reduction of the NCC lifetime, because the cross-section of the hole capture for those defects is much larger than that for V_2 ones. Then, the following question arises: Why do defects V_2 and V_2O, which possess electron levels close to each other in their forbidden gaps, have such different recombination properties? However, this issue demands additional study.

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Received 15.05.06.
Translated from Ukrainian by O.I. Voitenko

ПРО ПРИРОДУ "НЕГАТИВНОГО" ВІДПАЛУ ЧАСУ ЖИТТЯ НЕРІВНОВАЖНИХ НОСІЇВ ЗАРЯДУ В ОПРОМІНЕНОМУ n-Si

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Р е з ю м е

Досліджено зміну рекомбінаційних властивостей опроміненого γ-квантами ^{60}Co кремнію n-типу провідності, вирощеного методом Чохральського (Cz n-Si), при відпалі його у діапазоні температур 20 — 350 °C, а також в результаті опромінення електронами з енергією 1 МеВ в цьому ж температурному діапазоні. Встановлено, що зменшення часу життя τ нерівноважних носіїв заряду (ННЗ) після відпалу у діапазоні 200 — 300 °C ("від'ємний" відпал) зумовлено утворенням V_2O комплексів ($V_2 + O \rightarrow V_2O$). При утворенні V_2O час життя ННЗ зменшується внаслідок того, що переріз захоплення дірок цими дефектами значно більший, ніж дефектами V_2. Показано, що утворення і відпал комплексів V_2O відбувається з енергіями активації 1,35 і 1,6 еВ відповідно, а поперечний переріз захоплення дірок цими комплексами $\sigma_p = 3{\cdot}10^{-13}$ см^2.