M.M. KRAS'KO, A.G. KOLOSIUK, V.V. VOITOVYCH, V.YU. POVARCHUK,
I.S. ROGUTS'KYI

Institute of Physics, Nat. Acad. of Sci. of Ukraine
(46, Nauky Ave., Kyiv 03680, Ukraine; e-mail: krasko@iop.kiev.ua)

INFLUENCE OF DIVACANCY-OXYGEN
DEFECTS ON RECOMBINATION PROPERTIES
OF n-Si SUBJECTED TO IRRADIATION
AND SUBSEQUENT ANNEALING

The variation of recombination properties in n-Si grown by the Czochralski method, doped to the free electron concentration $n_0 \sim 10^{14} \div 10^{16}$ cm^{-3}, irradiated with ^{60}Co γ-quanta or 1-MeV electrons, and isochronously annealed for 20 min in the temperature interval 180–380°C, in which divacancy-oxygen (V_2O) complexes are formed and annealed, has been studied in detail. The nonequilibrium charge carrier lifetime τ is found to significantly decrease after the annealing in a temperature interval from 180 to 280°C, with the effect being stronger for low-resistive n-Si. It is shown that a change in τ after the annealing at 180–380°C is caused by divacancy defects, most probably V_2O. By analyzing the experimental data with the help of the Shockley–Read–Hall statistics, it is found that the formation of V_2O defects is characterized by an activation energy of 1.25 ± 0.05 eV and a frequency factor of $(1 \pm 0.5) \times 10^9$ s^{-1}, and their annealing by an activation energy of 1.54 ± 0.09 eV and a frequency factor of $(2.1 \pm 1.4) \times 10^{10}$ s^{-1}. The values of the hole capture cross-sections by singly and doubly charged acceptor states of V_2O are obtained as: $(5 \pm 2) \times 10^{-13}$ and $(8 \pm 4) \times 10^{-12}$ cm^2, respectively.

K e y w o r d s: gamma irradiation, divacancy-oxygen defect, charge carrier lifetime, silicon.

1. Introduction

Among the integral parameters of silicon, the lifetime of charge carriers, τ, is the most sensitive to the radiation action. As a rule, τ can vary by orders of magnitude in silicon irradiated with γ-quanta or a-few-MeV electrons, whereas the carrier concentration or mobility practically does not change at that. The degradation of τ in irradiated silicon is caused by the formation of radiation-induced defects, which are effective recombination centers [1–4]. That is why the application of radiation-induced defects as the centers of charge carrier recombination forms the basis of radiation-technological methods for the fabrication of power silicon-based devices. In general, the parameter τ in silicon is sensitive to the presence of various defects, which makes it a powerful tool to study the defect properties of this material and to control its quality [5].

In this work, our attention is focused on the influence of divacancy-oxygen (V_2O) defects on the recombination properties of n-Si. The V_2O complex was identified in EPR studies of electron-irradiated Cz Si as long ago as in 1976. However, the positions of its electron levels in the forbidden band were discovered recently, when V_2O was started to be considered as the main candidate responsible for the degradation of silicon detectors of ionizing particles [7, 8]. Now, it was found [9–16] that the annealing of irradiated Cz or diffusion oxygenated float-zone (DOFZ) silicon in the temperature interval 200–300°C leads to the interaction between a mobile divacancy V_2 and an interstitial oxygen atom O_i. As a result of this interaction, a V_2O defect is formed, which is annealed at temperatures of about 300–350°C. The transformation $V_2 \rightarrow V_2O$ occurs with a proportionality of $1:1$. In work [17], the electron level with an energy of $\sim E_c - 0.55$ eV was attributed to $V_2O(-/0)$. However, a detailed study of the V_2 annealing kinetics in Cz and DOFZ silicon revealed another spectrum of V_2O

levels. In particular, the electron levels of V_2 and V_2O turned out very similar. Two new levels in n-Si located at $\sim E_c - 0.23$ eV and $\sim E_c - 0.47$ eV were associated with doubly and singly charged acceptor states of V_2O [9–12]. A new level at $\sim E_v + 0.23$ eV in p-Si was identified as a donor state of $V_2O(+/0)$ [13–16]. At the same time, the level at $\sim E_v + 0.08$ eV is considered as $V_2O(2+/+)$ [14, 16].

Most of the above-mentioned researches were aimed at studying the electron properties of V_2O. The influence of these defects on the variation of integral parameters (in particular, the charge carrier lifetime) of Cz Si remains almost unstudied. Nevertheless, the data in works [18, 19] testify to a relation between the changes of τ and the formation of V_2O defects in Cz n-Si crystals ^{60}Co γ-irradiated and annealed in a temperature interval of about 200–400 °C, as well as in the case of electron irradiation in the same temperature interval. Being characterized by a high thermal stability and having deep levels in the forbidden Si region, V_2O defects can serve as effective recombination centers in silicon and silicon-based devices.

In this paper, we studied the degradation of the lifetime of nonequilibrium charge carriers in ^{60}Co γ-irradiated and 1-MeV-electron-irradiated Cz n-Si ($n_0 \sim 10^{14} \div 10^{16}$ cm^{-3}) after its isochronous annealing in a temperature interval of 20–380 °C. In this context, an interval of about 180–380 °C was analyzed in detail in order to determine the role of V_2O defects in the modification of Cz n-Si recombination properties.

2. Experimental Part

2.1. Experimental specimens

Two groups of n-type silicon specimens were used.

(i) n-Si : P. The phosphorus (P) impurity created the conductivity of the n-type in Si. Some specimens from this group had a high concentration of carbon impurities (n-Si : P,C).

(ii) n-Si : TD. Oxygen thermodonors (TDs) were responsible for the donor properties of Si specimens in this group. The n-Si : TD specimens were obtained by thermally treating the high-resistive n-Si ($P \sim 1 \times 10^{13}$ cm^{-3}) at 450 °C. The condition [TD]/[P] > 50 was obeyed at that. Thermodonors, unlike phosphorus atoms, are insensitive to irradiation. They do not create complexes with radiation-induced vacancies (like VP defects) and do not lose their donor activity under irradiation [20].

The specimen parameters (the initial concentrations of free electrons, n_0, oxygen, O_i, and carbon, C_s, as well as the lifetime τ_0 of nonequilibrium charge carriers before irradiation, are quoted in Table 1 for both groups.

2.2. Specimen irradiation and annealing

The experimental specimens were irradiated at room temperature with ^{60}Co γ-quanta to a dose of about 7×10^{14} cm^{-2} [the radiation intensity $J_\gamma \approx 2 \times 10^{11}$ quantum/(cm^2 s)] and 1-MeV electrons with to a dose of 1×10^{13} cm^{-2} [$J_e \approx 3 \times 10^{11}$ electrons/(cm^2 s)]. The irradiated specimens were isochronously (for 20 min) annealed in the air atmosphere in a temperature interval of 20–380 °C.

2.3. Measurement and analysis procedures

The lifetime of charge carriers in the specimens was determined from the nonequilibrium photoconductivity relaxation under low-excitation conditions ($\Delta n/n_0 \approx 1\%$). The determination error for τ did not exceed $\pm 10\%$. The influence of the irradiation and subsequent annealing was estimated, by using the known relation

$$\tau^{-1} = \tau_0^{-1} + k_\tau \Phi, \tag{1}$$

where τ_0 is the initial lifetime of nonequilibrium charge carriers, τ the lifetime of nonequilibrium charge carriers after the irradiation to the dose Φ and the subsequent annealing, and k_τ the τ-degradation constant.

The experimental results were analyzed with the help of the Shockley–Read–Hall statistics. In our case (n-Si, a low defect concentration, $\Delta n \ll n_0$, and

Table 1. **Specimen parameters**

Specimen	n_0, 10^{15} cm^{-3}	τ_0, μs	$[C_s]$, 10^{16} cm^{-3}	$[O_i]$, 10^{17} cm^{-3}
n-Si : P	~ 0.1	110–130	<5	6–9
	~ 1	80–90	<5	
	~ 2	120–130	<5	
	~ 5.5	90–100	<5	
	~ 1	50–60	~ 40	
n-Si : TD	~ 0.5	50–55	<5	8–9
	~ 1	55–60	<5	
	~ 8.5	75–80	<5	

the charge carrier recombination occurs through levels in the upper half of the band gap), the lifetime of nonequilibrium charge carriers is governed by the lifetime of holes (minority charge carriers in n-Si), and the following expression is valid for every recombination center:

$$\tau_i = (\sigma_{p,i} \upsilon_p [N_i])^{-1} \left[1 + \frac{N_c \exp(-E_i/k_B T)}{n_0} \right], \qquad (2)$$

where $\sigma_{p,i}$ is the hole capture cross-section by the i-th recombination center, υ_p the heat velocity of holes, N_i the concentration of the i-th center with the level E_i, N_c the effective density of states in the conduction band, k_B the Boltzmann constant, and T the absolute temperature. The total change of τ is determined as the sum of the partial contributions τ_i,

$$\tau^{-1} - \tau_0^{-1} = \sum_i \tau_i^{-1}. \qquad (3)$$

Then, from Eq. (1) and taking Eqs. (2) and (3) into account, the following expression is obtained for the degradation constant of the charge carrier lifetime:

$$k_\tau = \sum_i \sigma_{p,i} \upsilon_p \eta_i \left[1 + \frac{N_c \exp(-E_i/k_B T)}{n_0} \right]^{-1}, \qquad (4)$$

where $\eta_i = [N_i]/\Phi$ is the efficiency of the i-th recombination center formation.

3. Results and Their Discussion

In the general case, the change of τ in an irradiated and subsequently annealed silicon specimen means the annealing or the additional formation of the main recombination center or the formation of a new one, which is more recombinationally active than those formed after the irradiation. Therefore, the change of τ was studied firstly after the irradiation and then after the irradiation and subsequent annealing.

3.1. The change of τ
### in ^{60}Co γ-irradiated Cz n-Si

Figure 1 demonstrates the dose dependences of $\Delta\tau^{-1}$ for (*a*) n-Si:P and (*b*) n-Si:TD specimens with various free electron concentrations n_0 irradiated with ^{60}Co γ-quanta. One can see that $\Delta\tau^{-1}$ linearly depends on Φ for all specimens in both groups. This circumstance makes it possible to determine the experimental values of k_τ^{irr} with the help of expression
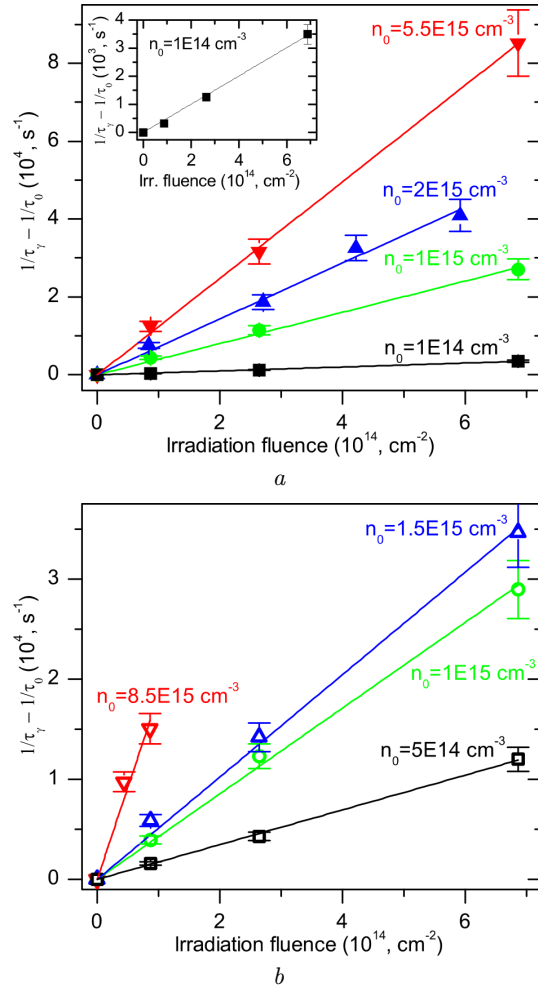
Fig. 1. Dependences of $\Delta\tau^{-1}$ on the irradiation fluence with ^{60}Co γ-quanta for n-Si:P (*a*) and n-Si:TD (*b*) specimens with various free electron concentrations n_0 (points correspond to experimental data, and solid curves to their linear approximations

(1). At the same time, the dependence $k_\tau^{\mathrm{irr}}(n_0)$ for the γ-irradiated n-Si:P and n-Si:TD specimens is increasing (see Fig. 2), and the experimental points for both n-Si groups lie on the same curve.

It is known that the vacancy-oxygen impurity atom complexes (VO or A-centers, an acceptor level of $E_c - 0.17$ eV) are the main recombination centers in ^{60}Co γ-irradiated Cz n-Si:P [4, 21–23] and n-Si:TD [22] at room temperature and a low excitation (injection). This fact is also confirmed by our calculations. The solid curve in Fig. 2 describes the contribution of VO-centers to the change of τ af-
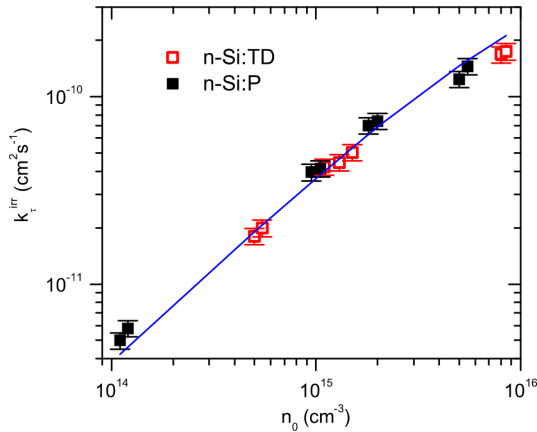
Fig. 2. Dependence of k_τ^{irr} on the free electron concentration n_0 for ^{60}Co γ-irradiated n-Si:P and n-Si:TD specimens. Symbols correspond to experimental data, the solid line is the calculated contribution of VO defects

ter the γ-irradiation calculated according to expression (4). When approximating the experimental dependence $k_\tau^{\mathrm{irr}}(n_0)$, the quantity $\sigma_{p,\mathrm{VO}}$ was the only fitting parameter, and the experimental value $\eta_{\mathrm{VO}} \approx \approx 4 \times 10^{-4}$ cm^{-1} for ^{60}Co γ-irradiated Cz n-Si specimens in both groups was taken from works [22, 23]. The calculation and experimental results are in good agreement, if $\sigma_{p,\mathrm{VO}} = (2.0 \pm 0.4) \times 10^{-13}$ cm^2, similarly to the results obtained in our previous [22] and other [3,23] researches. The growth of the dependence $k_\tau^{\mathrm{irr}}(n_0)$ in Fig. 2 occurs due to an increase in the occupation degree of the electron level of VO-centers in low-resistive specimens.

3.2. Change of τ in ^{60}Co γ-irradiated Cz n-Si at the isochronous annealing in a temperature interval of 20–380°C

3.2.1. Isochronous annealing

Figure 3 demonstrates the typical experimental dependences of k_τ on the isochronous (20 min) annealing temperature T_{ann} in an interval of 20–380°C for γ-irradiated Cz n-Si:P (a) and n-Si:TD (b) specimens with various free electron concentrations n_0. The main characteristic features are as follows.

• All $k_\tau(T_{\mathrm{ann}})$ dependences are qualitatively similar for Cz n-Si specimens in both groups and with different n_0-values. Annealing to about 180°C practically does not affect k_τ. Substantial changes occur in an interval of 180–380°C. Namely, k_τ drastically increases to $T_{\mathrm{ann}} \approx 240 \div 280$°C and, at the subsequent anneal-
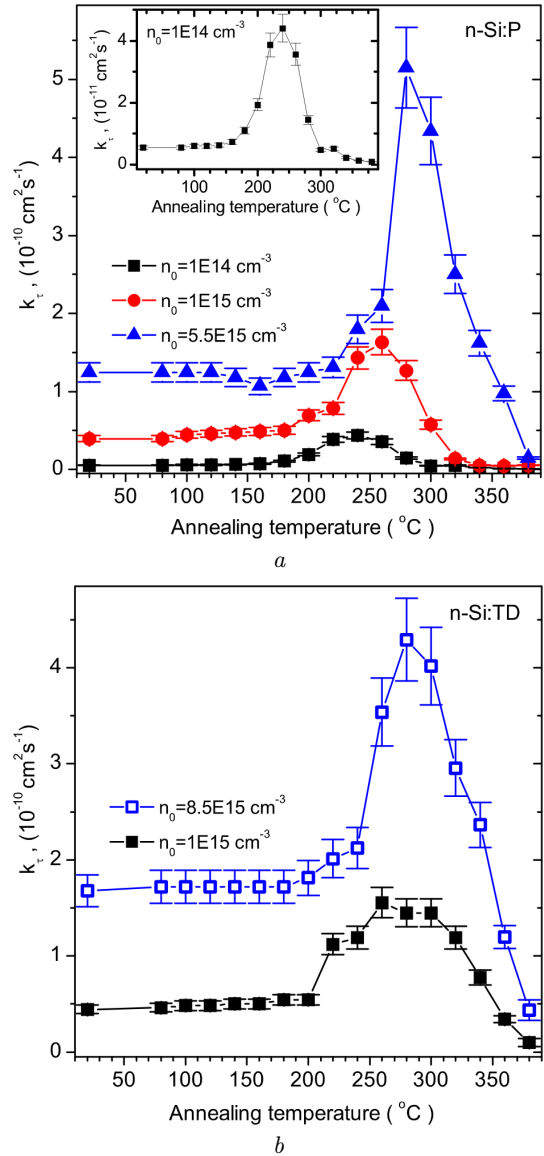
Fig. 3. Dependences of k_τ on the isochronous (20 min) annealing temperature for ^{60}Co γ-irradiated Cz n-Si:P (a) and n-Si:TD (b) specimens with various free electron concentrations n_0's

ing, decreases to a value corresponding to 80–90% of τ_0 at $T_{\mathrm{ann}} \approx 360 \div 380$°C. Note also that a peak-like change of k_τ in the interval from 180 to 380°C clearly correlates with the formation and annealing of V$_2$O defects in Cz n-Si (see Fig. 5 in work [11]).

• The height of the peak $\Delta k_\tau^{\mathrm{peak}} = k_\tau^{\mathrm{peak}} - k_\tau^{\mathrm{irr}}$ in the dependences $k_\tau(T_{\mathrm{ann}})$ is determined by the parameter n_0 (see Fig. 4). From Fig. 4 (curve *1*),

one can see that the growth of n_0 from 1×10^{14} to 8.5×10^{15} cm^{-3} induces an 8-fold increase of the peak height $\Delta k_\tau^{\text{peak}}$, which is stronger in low-resistive n-Si ($n_0 > 5 \times 10^{14}$ cm^{-3}). However, by comparing the absolute values of $\Delta k_\tau^{\text{peak}}$ in curve *1* in Fig. 4 and k_τ^{irr} in Fig. 2 in the examined n_0-interval, it is evident that the annealing effect on the τ-degradation in γ-irradiated Cz n-Si specimens is much more pronounced in high-resistive specimens. For example, the ratio $\Delta k_\tau^{\text{peak}}/k_\tau^{\text{irr}} \approx 10$ for specimens with $n_0 = 1 \times 10^{14}$ cm^{-3} and about 3 for specimens with $n_0 = 5.5 \times 10^{15}$ cm^{-3}.

• There is also a tendency that the peak shifts toward higher temperatures with the increase of n_0. In our case, this shift amounted to about 40°C (see Fig. 3, *a*).

3.2.2. The origin of τ variation at isochronous annealing

The degradation of τ in the T_{ann}-interval from 180 to 240–280°C (Fig. 3) testifies to the formation of either VO complexes (the major recombination centers after ^{60}Co γ-irradiation) or more efficient recombination centers. The temperature interval 180–300°C corresponds to the annealing interval of V_2 in Cz and DOFZ Si [9–16]. The efficiency of the VO center formation in ^{60}Co γ-irradiated Cz n-Si specimens at room temperature is approximately two orders of magnitude higher than that of the V_2 formation [1, 23]. Therefore, an additional formation of VO centers due to a possible dissociation of V_2 ($V_2 \rightarrow$ $\rightarrow$ V + V $\rightarrow$ VO) cannot change τ by an order of magnitude (or even by several times). Accordingly, the annealing of V_2 has to result in the formation of another defect of the divacancy nature, which is confirmed by the results of the following experiment.

A Cz n-Si specimen about 2.5 mm in thickness was irradiated with 1 MeV electrons from one of its largest faces at room temperature, whereas the lifetime was measured at both faces. A comparison of DLTS spectra obtained for them (see Fig. 1 in our work [24]) demonstrates that the peaks associated with singly ($E3$, $E_c - 0.42$ eV) and doubly charged ($E2$, $E_c - 0.23$ eV) acceptor V_2 states were registered only on the irradiated side of the specimen, whereas the peak of VO centers ($E1$, $E_c - 0.17$ eV) on the both sides, although the efficiency of the VO center formation on the shadow side was lower by almost an
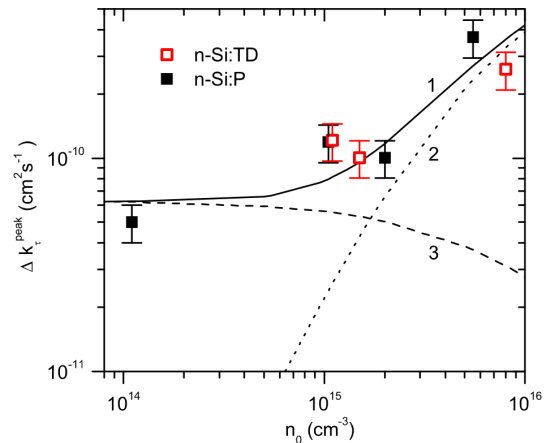

Fig. 4. Dependences of the peak height $\Delta k_\tau^{\text{peak}} = k_\tau^{\text{peak}} - k_\tau^{\text{irr}}$ in the dependences $k_\tau(T_{\text{ann}})$ (see Fig. 3) on n_0. Symbols correspond to experimental data; curves to the calculated contribution of V_2O defects: total (*1*), V_2O(2–/–) (*2*), V_2O(–/0) (*3*)
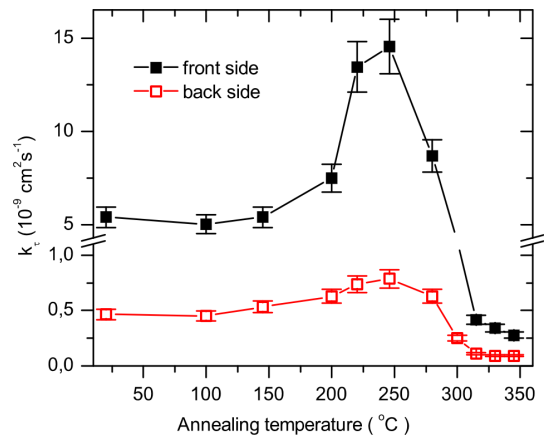
Fig. 5. Dependences of k_τ on the isochronous (20 min) annealing temperature for the front and back sides of the Cz n-Si:[$P \approx 1 \times 10^{15}$ cm^{-3}] specimen about 2.5 mm in thickness 1-MeV-electron-irradiated to the dose $\Phi = 1 \times 10^{13}$ cm^{-2}

order of magnitude. This fact means that the energy of electrons at the shadow side of the specimen was lower or close to the threshold energy of the V_2 formation. In this case, if the changes of τ in the interval from 180 to 380°C (Fig. 3) were induced by the divacancy defect, then they should not be observed at the shadow side of the specimen.

Figure 5 exhibits the experimental dependences $k_\tau(T_{\text{ann}})$ in the interval of 20–350°C measured for the specimen sides irradiated with 1-MeV electrons (the front side) and not (the back side). One can see
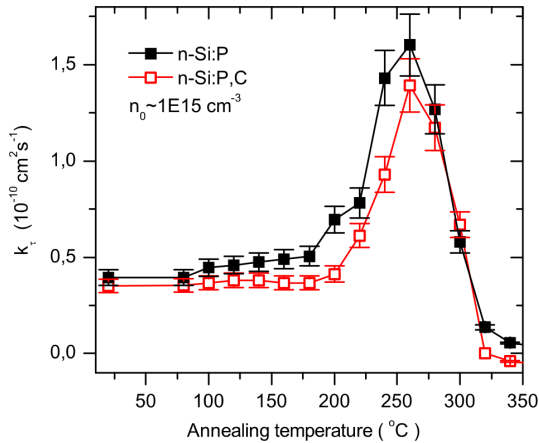
Fig. 6. Dependences of k_τ on the isochronous (20 min) annealing temperature for ^{60}Co γ-irradiated ($\Phi = 7 \times 10^{14}$ cm^{-2}) specimens with various carbon concentrations [C$_s$]: 4×10^{16} cm^{-3} for n-Si : P and 4×10^{17} cm for n-Si : P, C

that the ratio between the k_τ^{irr} values measured at those sides ($T = 20°$C in Fig. 5) is about an order of magnitude, being the same as the ratio for the VO formation efficiency in the DLTS spectra (see Fig. 1 in work [24]). It is important that, for the shadow side of the specimen, where V$_2$ were not observed in the DLTS spectra, the relative height of the $\left(k_\tau^{\mathrm{peak}} - k_\tau^{\mathrm{irr}}\right)/k_\tau^{\mathrm{irr}}$ peak is significantly smaller than for the irradiated one (about 0.5 and 2, respectively). The presence of a small peak in the dependence $k_\tau(T_{\mathrm{ann}})$ for the shadow side can be explained by the fact that DLTS measurements were carried out in the near-surface layer about 10 μm in thickness, whereas the recombination region size is about 0.15–0.50 mm, and the electron energy in this region is already higher than the threshold energy of the V$_2$ formation. Thus, the formation of new divacancy defects stimulates the degradation of τ at the specimen side irradiated with 1 MeV electrons (Fig. 5) and, accordingly, in γ-irradiated specimens (Fig. 3) at their isochronous annealing in a temperature interval of 180–300°C.

It is most probably that those defects are V$_2$O complexes. First, the DLTS study of the kinetics of V$_2$ annealing and V$_2$O formation in Cz and DOFZ n-Si shows that the transformation of V$_2$ into V$_2$O occurs with a proportionality of 1 : 1 [9–12]. Second, the variation of k_τ in the temperature interval from 180 to 380°C (Figs. 3 and 5) clearly correlates with the formation and annealing of V$_2$O defects in Cz n-Si

(see Fig. 5 in work [11]). In work [21] on the basis of the temperature dependences of τ in γ-irradiated and then annealed high-resistive Cz n-Si specimens ($n_0 = 7 \times 10^{13}$ cm^{-3}), it was shown that the τ degradation is driven by an acceptor with a level of $E_c - 0.45$ eV (supposedly, this is C$_i$O$_i$–V$_2$). However, the recent DLTS researches do not support this hypothesis. Moreover, the formation of C$_i$O$_i$-V$_2$ complexes in ^{60}Co γ-irradiated Cz n-Si to low doses is hardly probable, because the concentration of C$_i$O$_i$ complexes, as well as the concentrations of all other radiation-induced defects, is much lower than the concentration of O$_i$ (in our case, almost by six orders of magnitude). Note also that the level of this defect is practically the same as the position of V$_2$O($-$/0). Figure 6 demonstrates the experimental dependences $k_\tau(T_{\mathrm{ann}})$ for γ-irradiated Cz n-Si specimens with various C$_s$ concentrations. It is evident that the growth of [C$_s$] from about 4×10^{16} to 4×10^{17} cm^{-3} does not affect the behavior of τ annealing.

### 3.2.3. Analysis of τ variation at isochronous annealing

According to the results of our researches, the variation of τ in the dependences $k_\tau(T_{\mathrm{ann}})$ within a temperature interval of 180–380°C (see Fig. 3) takes place due to the formation (from 180 to 240–280°C) and annealing (from 240–280 to 380°C) of V$_2$O complexes. Then, in the examined case, the total changes of τ after the irradiation and subsequent annealing can be presented, according to expression (3), as the sum of the VO and V$_2$O contributions:

$$\tau^{-1} - \tau_0^{-1} = \tau_{\mathrm{VO}}^{-1} + \tau_{\mathrm{V_2O}(-/0)}^{-1} + \tau_{\mathrm{V_2O}(2-/-)}^{-1}, \qquad (5)$$

where the contribution of each defect is determined by formula (2). The system of kinetic equations that describes the processes of V$_2$O formation (V$_2$ + O $\rightarrow$ $\rightarrow$ V$_2$O) and annealing can be written in the form

$$\begin{cases} \dfrac{d[\mathrm{V_2}]}{dt} = -c_{\mathrm{V_2O}}[\mathrm{V_2}], \\[2mm] \dfrac{d[\mathrm{V_2O}]}{dt} = c_{\mathrm{V_2O}}[\mathrm{V_2}] - c_{\mathrm{V_2O}}^{\mathrm{ann}}[\mathrm{V_2O}], \end{cases} \qquad (6)$$

where $c_{\mathrm{V_2O}} = c_0 \exp\left[-E_a/\left(k_\mathrm{B}T\right)\right]$ and $c_{\mathrm{V_2O}}^{\mathrm{ann}} = c_0^{\mathrm{ann}} \exp\left[-E_a^{\mathrm{ann}}/\left(k_\mathrm{B}T\right)\right]$ are the constants of the V$_2$O complex formation and annealing, respectively.
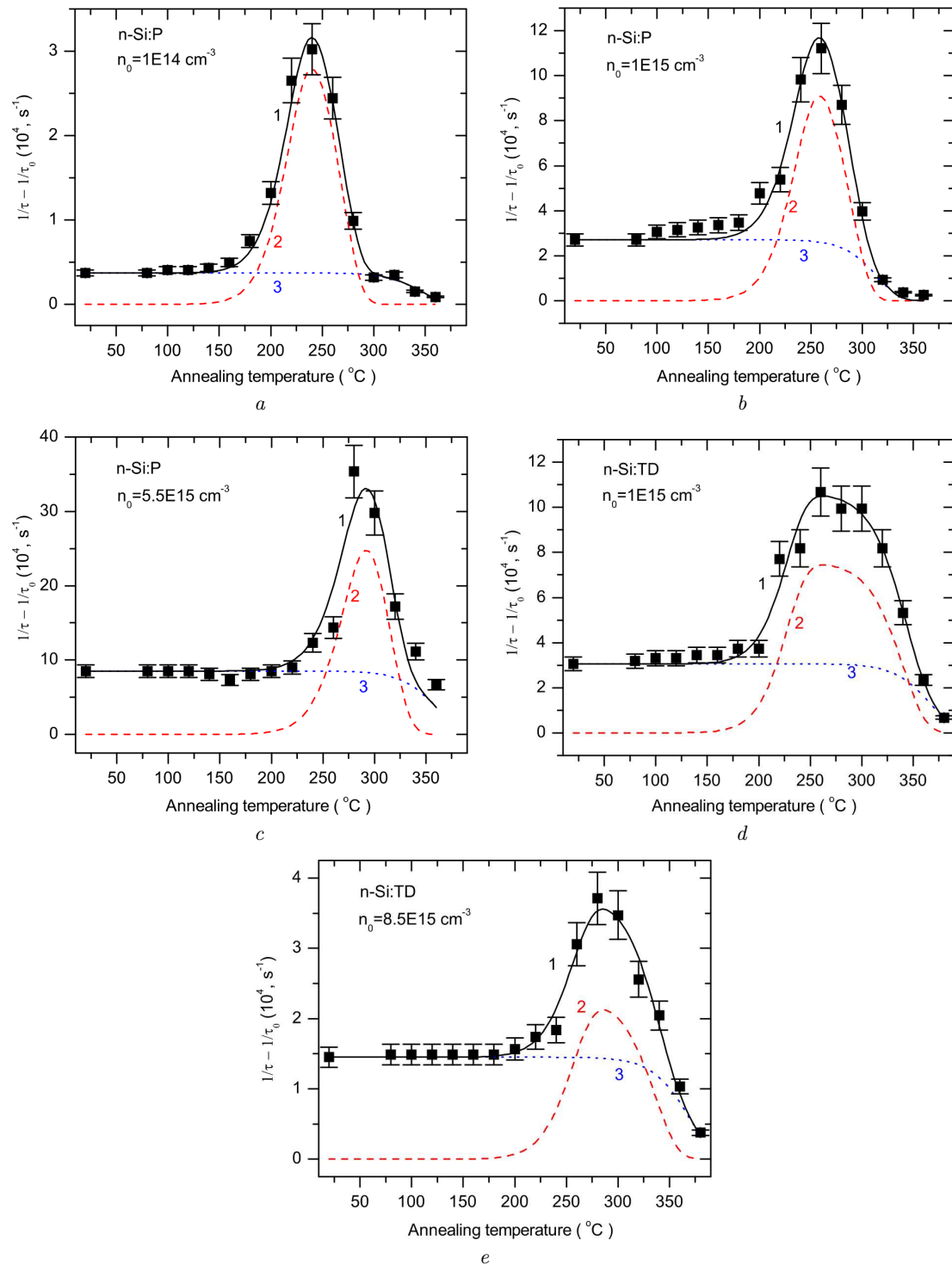
Fig. 7. Approximations (solid curves) of experimental dependences $\Delta\tau^{-1}(T_{\text{ann}})$ for ^{60}Co γ-irradiated Cz n-Si : P (panels a, b, and c) and n-Si : TD (panels d and e) sources: total contribution (1), V_2O (2), and VO (3)

Table 2. **Activation energies and frequency factors for the V₂O formation and annealing and the VO annealing**

Specimen	n_0, 10^{15} cm^3	V$_2$O formation		V$_2$O annealing		VO annealing	
		c_0, s^{-1}	E_a, eV	c_0, s^{-1}	E_a, eV	c_0, s^{-1}	E_a, eV
n-Si:P	$\sim$0.1	1.5×10^9	1.2	2.2×10^{10}	1.45	5.6×10^9	1.59
	$\sim$1	1.5×10^9	1.24	3.3×10^{10}	1.52	5.6×10^9	1.54
	$\sim$5.5	0.5×10^8	1.27	3.5×10^{10}	1.63	5.6×10^9	1.61
n-Si:TD	$\sim$1	1.5×10^9	1.23	7.5×10^9	1.56	5.6×10^9	1.64
	$\sim$8.5	1.2×10^9	1.29	1.3×10^{10}	1.6	5.6×10^9	1.64

Table 3. **Cross-sections of hole capture on V₂O and VO acceptor levels**

Defect	Level, eV	σ_p at 293 K, cm^2
VO($-$/0)	$E_c - 0.17$	$(2.0 \pm 0.4) \times 10^{-13}$
V$_2$O(2$-$/$-$)	$E_c - 0.23$	$(8 \pm 4) \times 10^{-12}$
V$_2$O($-$/0)	$E_c - 0.47$	$(5 \pm 2) \times 10^{-13}$

The solution of Eqs. (6) with the initial conditions $[V_2](t = 0) = [V_2]_{irr}$ and $[V_2O](t = 0) = 0$ is as follows:

$$[V_2O] = \frac{[V_2]_{irr}}{(c_{V_2O}^{ann}/c_{V_2O} - 1)} \times$$

$$\times \left(\exp(-c_{V_2O}t) - \exp(-c_{V_2O}^{ann}t) \right), \tag{7}$$

where t is the isochronous annealing time, $[V_2]_{irr}$ the concentration of divacancies after the irradiation, and $[V_2O]$ the total concentration of V$_2$O complexes, which is the sum of their concentrations in the singly and doubly charged negative states, because the Fermi level in our specimens is located above the V$_2$O($-$/0) level at room temperature.

Figure 7 demonstrates the experimental dependences $\Delta\tau^{-1}(T_{ann})$ obtained for ^{60}Co γ-irradiated Cz n-Si:P (panels a, b, and c) and n-Si:TD (panels d and e) specimens together with their description, by using expressions (5) and (2) with the fitting parameters of VO and V$_2$O defects quoted in Tables 2 and 3. The concentration of V$_2$O complexes was calculated with the help of expression (7). The required $[V_2]_{irr}$ value was calculated taking into account that the ratio $\eta_{VO}/\eta_{V_2} \approx 10^2$ for ^{60}Co γ-irradiated Cz n-Si [1, 23]. At $T_{ann} > 300$°C, the VO and V$_2$O complexes are annealed simultaneously. Therefore, in order to

correctly determine the V$_2$O parameters, we separated the influence of VO on τ. For this purpose, the annealing constant $c_{VO} = 5.6 \times 10^9 \exp\left[-1.7/(k_B T)\right]$ was taken from work [1] as the basic one, and only the E_a-value for the VO annealing was corrected according to our experimental data (see Table 2).

From Table 2, one can see that the average E_a-value for the V$_2$O formation equals 1.25 ± 0.05 eV for both Cz n-Si groups. This result is in good agreement with the data demonstrating that the processes of V$_2$ annealing [12, 25] and V$_2$O formation [12] are characterized by the same value $E_a \approx 1.3$ eV. The annealing of V$_2$O is characterized by the value $E_a^{ann} = 1.54 \pm 0.09$ eV (see Table 2) as in theoretical work [26], but it is lower than a value of about 2 eV obtained in experimental work [27]. We also obtained E_a and c_0 values similar to ours, when using the experimental dependences for the concentration changes of V$_2$ and V$_2$O complexes at the isochronous annealing of electron-irradiated Cz n-Si (see Fig. 5 in work [11]). Note also that there is a tendency for the activation energies of V$_2$O formation and annealing to grow with n_0 (Table 2), which correlates with the shift of the k_τ^{peak} peak toward higher annealing temperatures (Fig. 3). It is evident that the V$_2$O charge state can play a key role in this situation. This issue is not considered in this paper.

The dependence $\Delta k_\tau^{peak}(n_0)$ (curve *1* in Fig. 4) corresponds to the maximum contribution of V$_2$O to the total change of k_τ, when all V$_2$ are transformed into V$_2$O. In this case, the calculations show that τ is driven by the V$_2$O($-$/0) level in high-resistive n-Si ($n_0 < 5 \times 10^{14}$ cm^{-3}, curve *3* in Fig. 4) and the V$_2$O (2$-$/$-$) level in low-resistive n-Si ($n_0 > 5 \times 10^{14}$ cm^{-3}, curve *2* in Fig. 4). The dependence $\Delta k_\tau^{peak}(n_0)$ grows

due to the increase in the electron occupation of the V_2O $(2-/-)$ level, for which σ_p is larger than for the V_2O $(-/0)$ one (see Table 3). At the same time, the total contribution of V_2O (curve *1* in Fig. 4) to the degradation of τ in the examined n_0-interval is much larger than that of VO (the main recombination center in ^{60}Co γ-irradiated Cz n-Si, Fig. 2), despite that the formation efficiency of primary V_2 (and, accordingly, the V_2O concentration maximum) is approximately two orders of magnitude smaller than the formation efficiency of VO. However, the large value of η_{VO} is compensated (i) in high-resistive n-Si by a low filling degree of the VO acceptor level by electrons (about 10^{-3} at $n_0 = 1 \times 10^{14}$ cm^{-3}), whereas $\sigma_{p,VO} \sim \sigma_{p,V_2O(-/0)}$, and (b) in low-resistive n-Si by the fact that $\sigma_{p,V_2O(2-/-)} > \sigma_{p,VO}$.

4. Conclusion

To summarize, it is found that the lifetime of nonequilibrium charge carriers in Cz n-Si irradiated either with ^{60}Co γ-quanta or 1-MeV electrons significantly decreases after the isochronous annealing within a temperature interval of about 180–280°C, with the efficiency of this process depending on n_0. Using specimens with various impurity compositions, but having the conductivity of the n-type, we have shown that the modification of recombination properties in Cz n-Si specimens firstly irradiated and then annealed in a temperature interval of 180–380°C is governed by the formation and annealing of V_2O complexes. By analyzing the experimental data with the use of the Shockley–Reed–Hall statistics, it is found that the formation and annealing of V_2O complexes are characterized by an activation energies of 1.25 ± 0.05 eV and 1.54 ± 0.09 eV, respectively. We also determined the values of σ_p for singly and doubly charged V_2O acceptor states: $(5 \pm 2) \times 10^{-13}$ and $(8 \pm 4) \times 10^{-12}$ cm^2, respectively. We have also analyzed and compared the influence of V_2O and VO defects on k_τ in Cz n-Si specimens with the free electron concentrations within the interval $n_0 \sim 10^{14} \div 10^{16}$ cm^{-360}, which were subsequently subjected to the ^{60}Co γ-irradiation and annealing.

1. S.D. Brotherton, P. Bradley. Defect production and lifetime control in electron and γ-irradiated silicon. *J. Appl. Phys.* **53**, 5720 (1982)

2. A. Hallen, N. Keskitalo, F. Masszi, V. Nagl. Lifetime in proton irradiated silicon. *J. Appl. Phys.* **79**, 3906 (1996).

3. H. Bleichner, P. Jonsson, N. Keskitalo, E. Nordlander. Temperature and injection dependence of the Shockley–Read–Hall lifetime in electron-irradiated p-type silicon, *J. Appl. Phys.* **79**, 9142 (1996).

4. M. Kras'ko, A. Kraitchinskii, A. Kolosiuk, V. Voitovych, R. Rudenko, V. Povarchuk. Radiation damage of carrier lifetime and conductivity in Sn and Pb doped n-Si. *Solid State Phenom.* **205–206**, 323 (2014).

5. E. Gaubas, E. Simoen, J. Vanhellemont. Carrier lifetime spectroscopy for defect characterization in semiconductor materials and devices. *ECS J. Solid State Sci.* **5**, 3108 (2016).

6. Y.-H. Lee, J.W. Corbett. EPR studies of defects in electron-irradiated silicon: A triplet state of vacancy-oxygen complexes, *Phys. Rev. B* **13**, 2653 (1976).

7. M. Moll, H. Feick, E. Fretwurst, G. Lindstrom, C. Schutze. Comparison of defects produced by fast neutrons and ^{60}Co-gammas in high-resistivity silicon detectors using deep-level transient spectroscopy, *Nucl. Instrum. Meth. Phys. A* **388**, 335 (1997).

8. K. Gill, G. Hall, B. MacEvoy. Bulk damage effects in irradiated silicon detectors due to clustered divacancies. *J. Appl. Phys.* **82**, 126 (1997).

9. E. Monakhov, B. Avset, A. Hallen, B. Svensson. Formation of a double acceptor center during divacancy annealing in low-doped high-purity oxygenated Si. *Phys. Rev. B* **65**, 233207 (2002).

10. G. Alfieri, E. Monakhov, B. Avset, B. Svensson. Evidence for identification of the divacancy-oxygen center in Si. *Phys. Rev. B* **68**, 233202 (2003).

11. V. Markevich, A. Peaker, S. Lastovskii, L. Murin, J. Lindstrom. Defect reactions associated with divacancy elimination in silicon. *J. Phys.: Condens. Matter* **15**, S2779 (2003).

12. M. Mikelsen, E. Monakhov, G. Alfieri, B. Avset, B. Svensson. Kinetics of divacancy annealing and divacancy-oxygen formation in oxygen-enriched high-purity silicon. *Phys. Rev. B* **72**, 195207 (2005).

13. M.-A. Trauwaert, J. Vanhellemont, H. Maes, A.-M. Van Bavel, G. Langouche, P. Clauws. Low-temperature anneal of the divacancy in p-type silicon: A transformation from V_2 to V_xO_y complexes? *Appl. Phys. Lett.* **66**, 3056 (1995).

14. V. Markevich, A. Peaker, B. Hamilton, S. Lastovskii, L. Murin, J. Coutinho, V.J.B. Torres, L. Dobaczewski, B.G. Svensson. Structure and electronic properties of trivacancy and trivacancy-oxygen complexes in silicon. *Phys. Status Solidi A* **208**, 568 (2011).

15. N. Ganagona, B. Raeissi, L. Vines, E. Monakhov, B. Svensson. Formation of donor and acceptor states of the divacancy–oxygen centre in p-type Cz-silicon. *J. Phys.: Condens. Matter* **24**, 435801 (2012).

16. V. Markevich, A. Peaker, B. Hamilton, S. Lastovskii, L. Murin. Donor levels of the divacancy-oxygen defect in silicon. *J. Appl. Phys.* **115**, 012004 (2014).

17. I. Pintilie, E. Fretwurst, G. Lindstrom, J. Stahl. Close to midgap trapping level in ^{60}Co gamma irradiated silicon detectors. *Appl. Phys. Lett.* **81**, 165 (2002).

18. M. Kras'ko, A. Kraitchinskii, V. Neimash, A. Kolosiuk, L. Shpinar. On the nature of "negative" annealing of the nonequilibrium charge carrier lifetime in irradiated *n*-Si, *Ukr. J. Phys.* **52**, 162 (2007).

19. V. Markevich, A. Peaker, S. Lastovskii, V. Gusakov, I. Medvedeva, L. Murin. Formation of radiation-induced defects in Si crystals irradiated with electrons at elevated temperatures. *Solid State Phenom.* **156–158**, 299 (2010).

20. V. Neimash, V. Siratskii, M. Sosnin, V. Shakhovtsov, V. Shindich. The thermal donors influence on radiation defecting in silicon, *Fiz. Tekh. Poluprovodn.* **23**, 250 (1989) (in Russian).

21. I. Kolkovskii, P. Lugakov, V. Shusha. Charge-carrier recombination in silicon irradiated with γ-rays of different energies. *Phys. Status Solidi A* **83**, 299 (1984).

22. M. Kras'ko, V. Neimash, A. Kraitchinskii, A. Kolosiuk, O. Kabaldin. Influence of A- and E-centers on the lifetime of nonequilibrium charge carriers in γ-irradiated *n*-Si. *Ukr. J. Phys.* **53**, 683 (2008).

23. A. Zubrilov, S. Koveshnikov, Effect of impurity composition of n-type Si on the radiation-induced defect formation and degradation of minority-charge-carrier lifetime under γ-irradiation. *Fiz. Tekh. Poluprovodn.* **25**, 1332 (1991) (in Russian).

24. M.-L. David, E. Simoen, C. Claeys, V. Neimash, M. Kras'ko, A. Kraitchinskii, V. Voytovych, A. Kabaldin, J.F. Barbot. On the effect of lead on irradiation induced defects in silicon. *Solid State Phenom.* **108–109**, 373 (2005).

25. P. Pellegrino, P. Lévêque, J. Lalita, A. Hallé, B.G. Svensson. Annealing kinetics of vacancy-related defects in low-dose MeV self-ion-implanted *n*-type silicon, *Phys. Rev. B* **64**, 195211 (2001).

26. J. Coutinho, R. Jones, S. Öberg, P. Briddon. The formation, dissociation and electrical activity of divacancy-oxygen complexes in Si. *Physica B* **340–342**, 523 (2003).

27. M. Mikelsen, J. Bleka, J. Christensen, E. Monakhov, B. Svensson. Annealing of the divacancy-oxyge and vacancy-oxygen complexes in silicon. *Phys. Rev. B* **75**, 155202 (2007).

М.М. Красько, А.Г. Колосюк,
В.В. Войтович, В.Ю. Поварчук, І.С. Рогуцький

ВПЛИВ ДЕФЕКТІВ
ДИВАКАНСІЯ-КИСЕНЬ НА РЕКОМБІНАЦІЙНІ
ВЛАСТИВОСТІ *n*-Si ПІСЛЯ ОПРОМІНЕННЯ
ТА НАСТУПНОГО ВІДПАЛУ

Р е з ю м е

Детально досліджено зміну рекомбінаційних властивостей опроміненого γ-квантами ^{60}Co чи 1 МеВ електронами кремнію *n*-типу провідності з концентрацією вільних електронів $n_0 \sim 10^{14}$–10^{16} см$^{-3}$, вирощеного методом Чохральського (Cz *n*-Si), після ізохронного відпалу в температурному діапазоні 180–380 °C, в якому відбувається утворення та відпал комплексів дивакансія-кисень (V$_2$O). Виявлено, що час життя нерівноважних носіїв заряду (τ) суттєво зменшується після відпалу в діапазоні $\sim$180–280 °C і цей ефект є сильнішим у низькоомному *n*-Si. Показано, що зміна τ після відпалу в діапазоні 180–380 °C зумовлена дефектом дивакансійної природи, найімовірніше V$_2$O. Було визначено, аналізуючи експериментальні дані за допомогою статистики Шоклі–Ріда–Холла, що утворення V$_2$O характеризується енергією активації $E_a = 1{,}25 \pm 0{,}05$ еВ і частотним фактором $c_0 = (1 \pm 0{,}5) \cdot 10^9$ с$^{-1}$, а їх відпал – енергією активації $E_a^{ann} = 1{,}54 \pm 0{,}09$ еВ і частотним фактором $c_0^{ann} = (2{,}1 \pm 1{,}4) \cdot 10^{10}$ с$^{-1}$. Також отримано значення поперечного перерізу захоплення дірок (σ_p) одно- і двозарядними акцепторними станами V$_2$O: $(5 \pm 2) \cdot 10^{-13}$ і $(8 \pm 4) \cdot 10^{-12}$ см^2 відповідно.