INFLUENCE OF THE CHARGE STATE OF NONEQUILIBRIUM VACANCIES ON THE FORMATION AND ANNEALING KINETICS OF RADIATION-INDUCED DEFECTS IN n-Si CRYSTALS

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The influence of the charge state of nonequilibrium vacancies on the processes occuring in n-Si crystals during their irradiation and heat treatment has been studied. The n-Si specimens with the electron concentration of $1 \times 10^{13} - 2 \times 10^{14}$ cm^{-3} prepared by the method of zone melting were studied. The irradiated crystals were investigated by the Hall and the local irradiation methods with subsequent measurements of the bulk photovoltage emerging across the irradiated part of the specimen. The researched specimens were irradiated with 2-MeV electrons or 25-MeV protons at a temperature of 300 K. It has been shown that the nature, energy spectrum, as well as the formation and annealing kinetics of radiation-induced defects in n-Si crystals depend on the charge states of nonequilibrium vacancies, doping impurities, and regions of disordering.

Using the method of local irradiation with subsequent measurements of the bulk photovoltage $U_{\rm ph}$ across the irradiated part of a specimen, the authors of works [1–3] demonstrated that primary radiation-induced defects (RIDs) obtained in p-Si crystals at a temperature of 300 K are charged positively. In n-Si crystals, interstitial atoms and vacancies are carriers, respectively, of positive and negative charges.

During the irradiation, nonequilibrium vacancies react quasi-chemically with doping (phosphorus or boron atoms) or background (oxygen or carbon ones) impurities, or with one another. As a result, secondary RIDs with high thermal stability are formed, which govern physical properties of the irradiated crystal up to 600°C (at this temperature, the secondary RIDs are annealed to the end).

It is well known [4] that A-centers ($E_c - 0.17$ eV), E-centers ($E_c - 0.44$ eV), divacancies (V_2, $E_c - 0.23$ and $E_c - 0.39$ eV), and V_2O complexes ($E_c - 0.5$ eV) are predominantly formed in n-Si crystals in the course of irradiation. At high exposition dozes or in the course of annealing, phosphorus- (PV_n) [5] and oxygen-containing (OV_n) [6] multivacancy defects can be formed. The formation of the latter is connected not only with the enhancement of diffusion processes, but seemingly also with a variation of the charge state of nonequilibrium vacancies in the process of annealing.

This work aims at studying the influence of a charge state of primary RIDs, in particular vacancies, on the nature, energy spectrum, and kinetics of accumulation and annealing of the secondary RIDs.

1. Methods of Experiment

The n-Si crystals fabricated by the method of zone melting with the concentration of electrons $N = 6 \times 10^{13}$ cm^{-3} were studied. The concentrations of background impurities (oxygen and carbon) determined from IR-absorption spectra were $N_{\rm O} \approx N_{\rm C} \approx 2 \times 10^{16}$ cm^{-3}. The density of growth dislocations was determined by analyzing etching pits and did not exceed $10^3 - 10^4$ cm^{-2}. The studied $1 \times 3 \times 10$ mm^3-specimens were irradiated with 2-MeV electrons or 25-MeV protons over the whole volume. The electron beam density was $\varphi_e = 5 \times 10^{12}$ cm^{-2} s^{-1}, and the proton beam density was $\varphi_p = 10^{11}$ cm^{-2} s^{-1}. Then the specimens exposed to radiation were isochronically annealed, i.e. subjected to a series of annealing cycles with equal duration, within the temperature interval 80—600 °C. The time interval of each isochronical annealing (IA) cycle at a fixed temperature was 10 min. After every IA cycle, the electron concentration N was measured within the interval 77—300 K. Measurements were carried out in a magnetic field of 10 kOe using the compensation method. In strongly compensated specimens, the energy levels of defects ΔE were determined from the slopes of the dependences $N = f(10^3/T)$. The measurement error of those values did not exceed 10%.

If $N > N'$, where N' is the concentration of electrons captured at acceptor levels of all RIDs, then one can determine the concentration of various RIDs from the plots $N(10^3/T)$ and $N(T_{\rm ann})$, where $T_{\rm ann}$ is the annealing temperature of irradiated crystals.

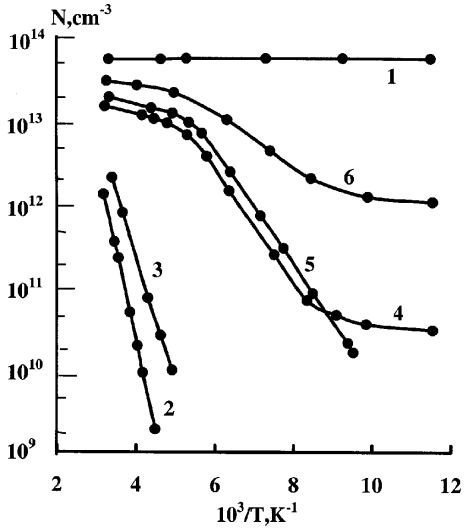

Fig. 1. Dependences of the electron concentration N in n-Si crystals on the temperature before (*1*) and after irradiation with 25-MeV protons: $\Phi_1 = 8.1 \times 10^{12}$ cm^{-2} (*2*, *3*), $T_{\rm ann} = 150$ °C (*4*), $T_{\rm ann} = 300$ °C (*6*), and $\Phi_2 = 2.7 \times 10^{12}$ cm^{-2} (*5*)

The concentration of A-centers N_A was determined as a difference ΔN of the concentrations of conduction electrons in the exhaustion ranges of A-centers ($T \approx 250$ K) and P-atoms ($T \approx 100$ K): $N_A = N(250\ {\rm K}) - N(100\ {\rm K})$; see Fig. 1, curves *4* and *5*, respectively.

The annealing of E-centers was completed at $T_{\rm ann} \approx 150$ °C. Therefore, when comparing curves *3* and *4* in Fig. 1, the concentration N_E of E-centers can be determined. An E-center, when being formed, is known [4] to remove two electrons from the conduction band. Therefore, $N_E = \Delta N(250\ {\rm K})/2$.

The concentration of divacancies N_{V_2} is defined by a variation of the electron concentration at 250 K during the IA procedure in the range 150—300 °C (Fig. 1, curves *4* and *6*). A divacancy is known [4] to capture one electron from the conduction band at $T = 300$ K; therefore, $N_{V_2} = \Delta N(250\ {\rm K})$. A further increase of N at 250 K in the course of IA ($T_{\rm ann}$=300÷600 °C) up to the initial value corresponds to the annealing of complex defects which are formed upon the irradiation (V_2+O) or annealing (PV_2 or PV_3) [5].

A certain number of researched specimens, $1 \times 3 \times 20$ mm^3 in dimensions, underwent irradiation through a mask. The mask was fabricated of tungsten plates, was 5 mm in thickness, and had a 1-mm slit. The bulk photovoltage $U_{\rm ph}$ across the irradiated part of a specimen was measured. A strip of white, polychromatic light 0.1 mm in width, which was moved along the specimen at a speed of 2 mm/min, was used as a probe. It is known that $U_{\rm ph} \sim \partial\rho/\partial x$ and $\partial\rho/\partial x \sim N_{\rm RID}$, where $\partial\rho/\partial x$ is the gradient of the specific resistance and $N_{\rm RID}$ is the concentration of RIDs; then, $U_{\rm ph} \sim N_{\rm RID}$. Thus, on the basis of the $U_{\rm ph}$ value, it is possible to estimate the RID concentration. Investigated specimens with concentrations $N_1 = 1 \times 10^{13}$ cm^{-3}, $N_2 = 6 \times 10^{13}$ cm^{-3}, and $N_3 = 2 \times 10^{14}$ cm^{-3} were irradiated with 2-MeV electrons to a fixed doze $\Phi = 5 \times 10^{15}$ cm. Therefore, $U_{\rm ph} \sim \eta$, where η is the efficiency of the introduction of secondary RIDs. Measurements were carried out at 300 K, i.e. in the exhaustion range of A-centers. Consequently, the height of the potential barrier between the irradiated and non-irradiated parts of a specimen was determined by a variation of the concentration of deeper ($\Delta E > E_c - 0.3$ eV) acceptor centers (E-centers, divacancies V_2).

2. Results

Within the range $T = 77 \div 300$ K, the dependences $N(10^3/T)$ in initial specimens corresponded to the full ionization of shallow donors (P atoms) with the concentration $N_{\rm P} = 6 \times 10^{13}$ cm^{-3} = const (Fig. 1, curve *1*). After the proton irradiation with the doze $\Phi = 2.7 \times 10^{12}$ cm^{-2}, the temperature dependence of the electron concentration corresponded to the exhaustion of acceptor centers with $E_c - 0.17 \pm 0.01$ eV (Fig. 1, curve *5*). If crystals were exposed to the doze $\Phi = 8.1 \times 10^{12}$ cm^{-2}, a linear section in the dependence $N(10^3/T)$ was observed, which either corresponds to the exhaustion of acceptor centers $E_c - 0.44 \pm 0.02$ eV (Fig. 1, curve *3*) or is connected with the presence of acceptor centers with a level $E_c - 0.54 \pm 0.01$ eV (Fig. 1, curve *2*). It is known [7] that the acceptor level $E_c - 0.17$ eV belongs to A-centers, the level $E_c - 0.44$ eV to E-centers or to V_2-divacancies, and the level $E_c - 0.54$ eV to unknown centers, the annealing temperature of which coincides with that of divacancies [4].

As is seen from Fig. 2 (curve *1*), after IA, the concentration of A-centers in the samples irradiated with 2-MeV electrons to the doze $\Phi = 1.5 \times 10^{14}$ cm^{-2} grew if $T_{\rm ann}$ was within the interval 90—120 °C, did not vary at $T_{\rm ann}$=120÷290 °C, and diminished as $T_{\rm ann}$ grew further (at 290 °C, the dissociation of the above-mentioned centers began). The annealing of V_2-divacancies in these crystals began at 250 °C (Fig. 2, curve *2*).

The concentration of A-centers in the crystals irradiated with 25-MeV protons to low dozes ($\Phi = 2.7 \times 10^{12}$ cm^{-2}) did not vary at the dissociation of E-centers. The annealing temperature $T_{\rm ann}$ of A-centers

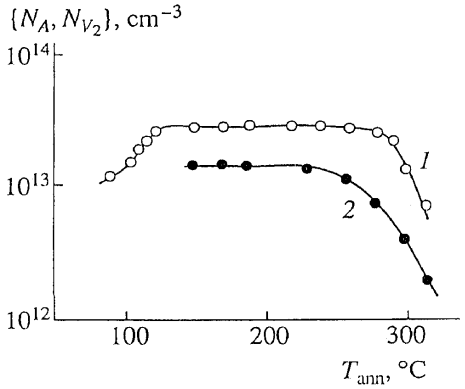

Fig. 2. The A-center (*1*) and divacancy (*2*) concentrations as functions of the isochonous annealing (IA) temperature in n-Si crystals irradiated with 2-MeV electrons

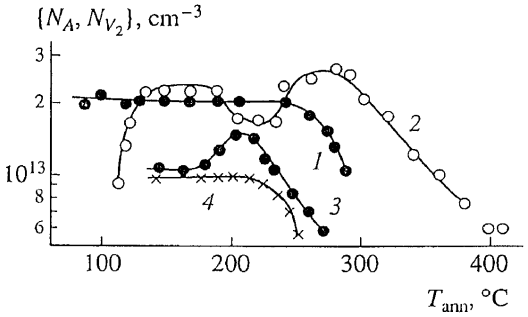

Fig. 3. Dependences of the A-center (*1,2*) and divacancy (*3,4*) concentrations in n-Si crystals irradiated with 25-MeV protons on the IA temperature. The radiation doze $\Phi = 2.7 \times 10^{12}$ (*1, 4*) and 8.1×10^{12} cm^{-2} (*2,3*)

and V_2-divacancies decreased down to 250 and 220°C, respectively (Fig. 3, curves *1* and *4*).

The concentration of A-centers in the specimens irradiated with high proton dozes ($\Phi = 8.1 \times 10^{12}$ cm^{-2}) grew in the temperature range of the E-center decay. It diminished at T_{ann} within the range 190–220°C; in the interval 240–300°C, negative annealing was observed; and, in the temperature interval 300–400°C, A-centers were annealed once and for all (Fig. 3, curve *2*). In the range 190–210°C, an increase of the V_2 concentration was observed. The start annealing temperature of V_2 decreased down to 210°C (Fig. 3, curve *3*).

The researches showed that the dependence $\eta_{E,V_2}(\varphi)$ of the efficiency of the introduction of E-centers and V_2-divacancies on φ had a maximum which shifted towards larger values of φ when N increased. In the crystals with the concentrations N_1, N_2, and N_3, the maximum point of φ_c was equal to 2×10^{12}, 5×10^{12}, and 1×10^{13} cm^{-2} s^{-1}, respectively (Fig. 4, curves *1*, *2*, and *3*).

3. Discussion of Results

In work [8], it was shown that $\eta_E/\eta_A \leq 10^{-2}$ in Si crystals irradiated with γ-quanta. At the same time, in the researched n-Si crystals irradiated with 2-MeV electrons, $\eta_E/\eta_A = 0.7$ in spite of the fact that N_O is approximately three orders of magnitude as large as N_P. Approximately the same value of this ratio was obtained in work [9] . In the opinion of the authors of work [10], the high efficiency of the introduction of E-centers at 300 K is caused by the influence of a charge state of vacancies on the speed of their migration and by the Coulomb interaction between an electron captured by a vacancy and a positively charged donor P^+.

Reasoning from the aforesaid, a conclusion that the charge state of primary RIDs governs the processes occurring in n-Si crystals at irradiation or annealing can be made.

As is known, in the course of irradiation at 300 K, A-centers are formed according to the reaction

$$V^- + O \rightarrow A^O + e^-. \quad (1)$$

The energy level $\Delta E_A = E_c - 0.17$ eV corresponds to A-centers. They are in the electroneutral state at 300 K and can react quasi-chemically with V^-: $A^O + V^- \rightarrow (V_2 + O)^-$. These new centers are related to the level $\Delta E_{V_2+O} = E_c - 0.5$ eV. At 300 K, they are charged negatively and, owing to the electrostatic interaction, their reaction with V^- is improbable.

In the researched specimens, the concentrations N_P, N_A, and N_{V_2+O} are within the interval $(2 \div 6) \times 10^{13}$ cm^{-3}, being three orders of magnitude as low as N_O. Similarly to P atoms, A-centers and V_2O-complexes could also have participated in quasi-chemical reactions with negative monovacancies if they had been charged positively. The efficiency of the introduction of RIDs is likely to be defined not only by quantitative relations among point defects that enter the quasi-chemical reaction, but by their charge state as well.

Since E-centers are charged negatively at room temperature ($\Delta E_E = E_c - 0.44$ eV), the formation of a two-vacancy center through the attachment of V^- is practically impossible. The attachment of V^- to V_2^- is also impeded, because $\Delta E_{V_2} = E_c - 0.39$ eV. At 300 K, they are charged negatively too. It should be noted that the formation of V_2 from negative monovacancies through the diffusion mechanism in the course of the

irradiation at 300 K is improbable. They are likely formed as primary defects.

Really, as is seen from Fig. 1, E-centers, divacancies, and V_2+O-complexes are formed in n-Si obtained by the zone melting and subjected to the proton irradiation at 300 K. We did not succeed in finding the level of $E_c - 0.5$ eV corresponding to the V_2+O-complex, although the availability of such a defect is evidenced for by an increase of the electron concentration measured at 250 K after IA in the range $T_{\rm ann} \geq 500$ °C [10].

The increase of the concentration of A-centers within the interval $T_{\rm ann} = 100 \div 150$ °C is explained by the interaction of vacancies that were released, when E-centers had decayed, with impurity atoms of oxygen. It should be emphasized that the ratio between the concentrations of dissociating and emerging again defects was $N_E/N_A = 0.7$ before annealing. Within the interval $T_{\rm ann}$ =230÷300 °C, i.e. in the divacancy decomposition range, no increase of N_A was observed, although $N_{V_2}/N_A = 0.6$ before annealing. In work [6], a stage of negative annealing was observed in Si crystals irradiated with 4-MeV electrons at $T_{\rm ann}$=230 °C; the authors explained this fact by the additional formation of A-centers at annealing of V_2. To all appearance, some divacancies were annealed following the reaction $V_2 + {\rm O} \to V_2{\rm O}$. Others dissociated and formed A-centers: $V + {\rm O} \to A$. The concentration N_{V_2} is much higher in Si crystals irradiated with 4-MeV electrons than that in ones exposed to 2-MeV electrons [7]. In work [6], therefore, an increase of N_A was observed during the annealing of divacancies.

The exhaustion of both E-centers and the second level of V_2 ($E_c - 0.39$ eV), as well as the dissociation of E-centers, occur simultaneously within the interval 100—150 °C. Therefore, it is impossible to trace the variation of N_{V_2} on the basis of the curves $N(10^3/T)$ obtained during the annealing of E-centers. Provided the dozes of irradiation with electrons are low ($\Phi = 1.5 \times 10^{14}$ cm^{-2}), vacancies which are formed at the decay of E-centers become charged negatively. It is possible to assume that, due to the electrostatic repulsion of negative vacancies and their capture by oxygen atoms, the efficiency of the introduction of V_2 should be negligibly small, and the concentration N_{V_2} should not increase (Fig. 2, curve *2*).

The fact that N_A remains constant in the crystals exposed to low dozes of protons ($\Phi = 2.7 \times 10^{12}$ cm^{-2}) and subjected to IA within the temperature interval 80–250 °C, is explained by the formation of disordered regions (DRs) which are effective drains for vacancies and reduce $T_{\rm ann}$ of the vacancy RIDs [7,11]. The DRs in n-Si are charged positively [12]; therefore, they capture negative vacancies with great efficiency and reduce both the probability of the additional formation and $T_{\rm ann}$ of A-centers (Fig. 3, curve *1*). For the same reason, $T_{\rm ann}$ of divacancies decreases down to 220 °C (Fig. 3, curve *4*). No increase of N_A was observed in the course of the V_2 decay.

The concentration of electrons in the conduction band is not high in crystals irradiated with high dozes of protons ($\Phi = 8.1 \times 10^{12}$ cm^{-2}). Therefore, at the initial stages of IA, by no means all the vacancies that are formed at annealing the E-centers become charged negatively, which can stimulate a decrease of the absorption efficiency of DR vacancies. Since $N_{\rm O} \gg N_{\rm DR}$, the supersaturation of a crystal by neutral monovacancies around $T_{\rm ann} = 120$ °C is cancelled by the formation of A-centers. A reduction of $T_{\rm ann}$ of A-centers down to 190 °C can be explained by the existence of DRs in the crystal bulk which are the effective drains for fragments appeared in the decay of A-centers, in particular vacancies which become charged negatively after the decay of E-centers ($T_{\rm ann} \geq 150$ °C) (Fig. 3, curve *2*).

Isolated DRs in Si crystals are annealed at 260°C. The appreciable annealing begins already at 200 °C [11]. The DRs seem to be the sources of divacancies at the initial stages of annealing, which may explain an increase of the concentration N_{V_2} at $T_{\rm ann}$=190÷210 °C (the formation of V_2-divacancies from separate monovacancies is hardly probable) (Fig. 3, curve *3*). Only monovacancies are seemingly the products of the DR decay as $T_{\rm ann}$ grows. The annealing of V_2-divacancies also begins in the impurity-defective part of the specimen, which results in the negative annealing of A-centers within the range $T_{\rm ann}$=230÷280 °C. The annealing of A-centers begins at 300 °C (Fig. 3, curve *2*).

The presence of a maximum on the curve of the dependence $\eta(\varphi)$ for n-Si crystals and its N-dependent displacement with respect to the φ-axis (Fig. 4, curves *1*, *2*, and *3*) allowed us to suppose that there is an optimum ratio between the concentrations of primary RIDs emerging per unit time and free electrons charging them.

As was noted above, it is A-centers, E-centers, and divacancies that predominantly emerge in n-Si crystals in the course of irradiation. Therefore, the relation

$$N_V = N_R + N_A + N_E + 2N_{V_2}$$

must be valid, where N_V is the total concentration of vacancies and N_R, N_A, N_E, and N_{V_2} are the concentrations of radiation-induced vacancies, emerging

A-centers, E-centers, and divacancies, respectively. From this equation, the total concentration of E-centers and divacancies, which are able, in the course of measurements, to change the electroresistance and, hence, the bulk photovoltage, is

$$N_E + N_{V_2} = N_V - N_R - N_A - N_{V_2}.$$

The initial concentration of vacancies is proportional to the irradiating electron beam density: $N_V \propto \varphi$. The concentrations of both the recombined vacancies and the formed A-centers are proportional to N_V and, therefore, $N_R \propto \varphi$ and $N_A \propto \varphi$ as well. So, for the first three terms on the right-hand side of relation (3), we have

$$N_V - N_R - N_A \propto \varphi.$$

Here, we assume that the charge states of vacancies do not influence practically the course of those processes.

However, identically (negatively) charged vacancies strongly repulse one another. For this reason, the formation of divacancies is possible only under the condition that at least one vacancy of the reacting pair should be in a neutral state. Therefore, $N_{V_2} \propto N_V N_{V^0}$, where N_{V^0} is the concentration of neutral vacancies. If the concentration of vacancies that have captured electrons is designated as N_{V^-}, then $N_{V^0} = N_V - N_{V^-}$. The quantity N_{V^-} is proportional, on the one hand, to N_V and, hence, to φ and, on the other hand, to the concentration of free electrons N, so that $N_{V^-} \propto N\varphi$. From here, it follows that $N_{V^0} \propto (1 - N/N_0)\varphi$, where N_0 is a definite constant ($N_0 > N$). As a result, the concentration of divacancies $N_{V_2} \propto (1 - N/N_0)\varphi^2$.

The quoted relations allow the character of the dependence of the bulk photovoltage in electron-irradiated n-Si on the parameters φ and N to be estimated qualitatively:

$$U_{\rm ph} \propto \frac{\varphi}{\varphi_0} - \left(1 - \frac{N}{N_0}\right)\left(\frac{\varphi}{\varphi_0}\right)^2.$$

Here, φ_0 is another constant ($\varphi_0 > 0$). It is easy to see that the function $U_{\rm ph}(\varphi)$ does possess a maximum. The maximum point

$$\varphi_{\max} = \frac{\varphi_0}{2(1 - N/N_0)}$$

shifts towards larger φ-values as the electron concentration N increases.

Thus, the nature and the energy spectrum of the secondary RIDs in n-Si crystals, as well as the kinetics of their annealing, are governed by charge states and a quantitative ratio between impurity atoms and nonequilibrium vacancies entering into a quasi-chemical reaction.

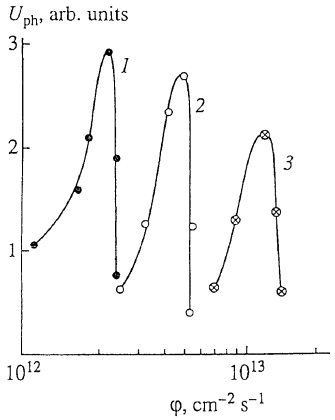

Fig. 4. Dependence of the bulk photovoltage $U_{\rm ph}$ on the electron beam density φ in locally irradiated n-Si crystals. The electron concentration N is 10^{13} (*1*), 6×10^{13} (*2*), and 2×10^{14} cm^{-3} (*3*). The energy of electrons in the beam is 2 MeV. The radiation doze $\Phi = 5 \times 10^{15}$ cm^{-2}

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ВПЛИВ ЗАРЯДОВОГО СТАНУ
НЕРІВНОВАЖНИХ ВАКАНСІЙ
НА КІНЕТИКУ УТВОРЕННЯ ТА ВІДПАЛУ
РАДІАЦІЙНИХ ДЕФЕКТІВ У КРИСТАЛАХ n-Si

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Р е з ю м е

Досліджено вплив зарядового стану нерівноважних вакансій на процеси, що протікають під час опромінення та термообробки в кристалах n-Si. Досліджували зразки n-Si, отримані методом зонної плавки, з концентрацією електронів 1x1013 – 2x1014 см -3. Опромінені кристали досліджували методами Холла та локального опромінення з наступним вимірюванням фото-ерс вздовж опроміненої частини зразка. Досліджувані зразки опромінювали електронами (E = 2 МеВ) або протонами (E = 25 МеВ) при температурі 300 К. Показано, що природа, енергетичний спектр, а також кінетика утворення та відпалу радіаційних дефектів в кристалах n-Si залежать від зарядового стану нерівноважних вакансій, легуючих домішок і областей розупорядкування.