

Interaction of defects and radiation properties of multicomponent semiconductors

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The effects of the absolute recombination zones and of the absolute squeezing of interacting lattice defects have been considered. The defect repulsion as well as their attraction has been shown to result both in a reduced asymptotic concentration of radiation-induced defects at high irradiation doses and in the increased radiation resistance of the materials at low doses. The analysis shows that the effects of stoichiometry deviations in two-component crystals influence considerably their radiation resistance while the selection of thermodynamic parameters makes it possible to control the number of the radiation-induced defects including the possibility of the radiation resistance improvement with respect to defects in both sublattices.

Рассмотрено влияние зон абсолютной рекомбинации и абсолютного вытеснения взаимодействующих дефектов решетки. Показано, что отталкивание дефектов так же, как и их притяжение приводит к уменьшению асимптотической концентрации радиационных дефектов при больших дозах облучения, так и к возрастанию радиационной стойкости материалов при малых дозах. Анализ показывает, что влияния отклонения от стехиометрии в двухкомпонентных кристаллах, существенно влияют на радиационную стойкость, а подбор термодинамических параметров синтеза кристаллов позволяет управлять количеством радиационных дефектов, включая возможность увеличения радиационной стойкости в отношении дефектов в обеих подрешетках.

The radiation resistance of semiconductor materials is a very actual technical problem, since it is necessary to provide stable working parameters of instruments operated under high radiation doses and intensities. The advances and prospects in the development of radiation-resistant metals have been reviewed in [1]. In [2, 3], the selection principles of non-metallic crystals for use as components of instruments intended for the stable operation under extremely great ionizing radiation doses had been formulated.

Besides of energetics, there is a wide variety of applied tasks requiring also the stable work of measuring setups and devices

under irradiation but within the range of much smaller irradiation doses. Those are medicine, custom service, etc. Many materials having the required parameters have been elaborated but in most cases those have not the necessary radiation resistance. The ways to process technologies of the known materials providing the retaining of the necessary parameters under irradiation are to be searched for.

In [4], the modern materials used as high-sensitive scintillators having rather high radiation resistance have been reviewed including in particular the semiconducting single crystals of zinc selenide. Is it possible to formulate the general principles

providing the radiation resistance improvement of the known semiconducting materials? It is just the problem that is considered in this work. It shall be shown in what follows that the radiation resistance is defined to a substantial extent by the pre-irradiation defects, the interaction of those with the radiation-induced ones is decisive for the ionizing irradiation results. Therefore, a brief review on the equilibrium and radiation-induced defect physics in crystalline compounds will be presented prior to formulate the specific task of this study.

1. Equilibrium and radiation point defects in crystalline compounds and instability zones

In monoatomic crystals (silicon, iron, copper, germanium, etc.), equilibrium lattice defects, namely, the Schottky vacancies and Frenkel pairs, are formed at any temperature differing from 0 K. The last-mentioned ones are separated pairs consisting of an interstitial atom (or ion), i , and a vacancy v in the lattice site leaven by the considered i . The equilibrium concentration of these defects is defined by the temperature and their formation energy. As to the Schottky defects, their formation energy is much lower, since the excess energy of an interstitial atom is very high. Therefore, it is just the Schottky vacancies rather than the Frenkel pairs that are predominant under equilibrium (except for few cases). The third equilibrium defect type has been found in crystals, too, unstable interstitial vacancy-atom pairs. Their nature is defined by the instability zones of the complementary defects (see [2]). It is just the Frenkel pairs $i-v$ that are generated under the radiation-induced interaction in equal concentrations ($c_i = c_v$). The further evolution of each defect is defined by its mobility in the lattice, temperature and interaction with other defects.

In crystalline compounds, in particular, in binary ones, as GaAs, CdS, ZnSe, the equilibrium lattice defects are formed also due to deviations from the stoichiometric ratios. The excess of one component is "dissolved" in the compound lattice, so that the "extra" atoms either become introduced into the lattice intersites or supplement their own sublattice, thus generating vacancies in the other one. The different defects contribute to different extents to the compound internal energy and entropy, their balance defining the predominance of one of

the mechanisms (see e.g. [2]). A combined mechanism is found also for the stoichiometry deviation when an excess of one component results simultaneously in the vacancy appearance in the other sublattice and the arise of the excess component interstitial atoms [5, 6].

The elementary interaction act between an ionizing radiation and a substance consists in the energy transfer from the attacking particle to one of the lattice atoms. If the transferred energy exceeds the Seitz threshold, the knocked out atom appears to be outside the first coordination sphere, it may form a metastable radiation-induced defect. Under action of heavy particles (including the relativistic heavy ones) when the energy transferred to the primary atom is very high, the collision cascades appear resulting in thermal peaks or spikes of displacements [7, 8].

In this work, it is just the fate of the radiation-induced point defects that we will restrict our study. The defects under consideration are formed under gamma and electron irradiation when the transferred energy results in the atom knocking out of the lattice site but the cascade-type disturbances are not arisen therein. In this case, the distribution of the radiation-induced defects can be considered as a spatially uniform one.

The study of the irradiation effects using the molecular dynamics methods [9] has shown that there is a specific zone near each vacancy (v) having a much lower mobility than that of interstitial atoms (i); every i getting to this zone recombines with v without activation. Such recombination instability zones (RIZ) have been found in numerous experiments. It has been shown (see [2]) that the RIZ are formed due to the superposition of the mobile defect periodic migration potential and the interaction potential of two defects. Analytical expressions for the RIZ size have been derived (see below). The instability zones have been shown to be formed also due to repulsion of two point defects but in this case, those are the absolute squeezing zones (SIZ). It has been established [10] that not only the RIZ (as it was believed before) but also the SIZ are of decisive importance in the accumulation of radiation-induced defects. As the SIZ and RIZ increase (other conditions being the same), the crystal radiation resistance increases. This is due to that the interstitial atoms displacing each other out of the SIZ favor the probability of their enter-

ing the RIZ of vacancies and thus stimulate the recombination, that is, the self-curing of the radiation-induced defects. The taking of SIZ into account results in a novel interpretation of all experimental data on the saturation doses in metals which have been elucidated to be not defined by the RIZ volume only but by the total RIZ and SIZ one. A generalized kinetic equation describing the accumulation of the radiation-induced defects under account for the pre-irradiation structure vacancies in metals has been proposed in [11] yet before the SIZ were taken into account.

This work is aimed at the study of the accumulation kinetics of point radiation-induced defects in binary semiconductors taking into account all the above-mentioned factors.

2. The radiation defects in binary crystals and kinetic equations describing their accumulation

For definiteness sake, the radiation defects in ZnSe crystals will be considered; nevertheless, the consideration will concern any binary compounds where the chemical bonds are of ionic character, at least to a little extent. The last is of importance for two reasons. The first consists in that the presence of oppositely-charged components forbids the so-called "anti-structure" substitutions, that is, the substitution of atoms of one sublattice by those of the other is impossible in the processes occurring in the crystal under irradiation. The second reason is that even in case of low share of ionicity of bonds their fast rupture results in that the particle leaves its site as an ion when the bond is broken under irradiation (see [2]). This provides the definiteness necessary for the analysis.

The specific features of the radiation-induced point defects in binary crystals as compared to the monoatomic ones are obvious: the vacancies arise in both sublattices and two kinds of interstitials are formed. To specify the situation for ZnSe, it is to note that each interstitial atom may occupy one of two interstitial positions, namely, the tetrahedral or octahedral one, having different crystal-chemical sizes. This defines different energies of elastic stresses in the lattice and, in its turn, the sizes of elastic RIZ and SIZ. The interstitial voids differing in their sizes are present in any crystal lattice and can be taken into account

separately; but we restrict ourselves by the assumption that all the interstitial positions are equivalent.

According to the Paragraph 1, when deriving the kinetic equations for the defect concentration variations in binary crystals under irradiation, the following is to be taken into account: (1) the stoichiometry deviations, i.e., the presence of pre-irradiation vacancies and/or interstitials of both components at concentrations c_{0v1} , c_{0v2} , c_{0i1} , c_{0i2} , respectively; (2) interaction with the radiation-induced defects having the current concentrations c_{v1} , c_{v2} , c_{i1} , c_{i2} , respectively, dependent on the irradiation dose Φ ; one has to bear in a mind of course that $c_{v1}(\Phi) = c_{i1}(\Phi)$ and $c_{v2}(\Phi) = c_{i2}(\Phi)$; (3) the RIZ formation due to interaction of complementary defects (with attractive potential) $i1-v1$ and $i2-v2$; (4) the SIZ formation due to interaction of defects of the same name (with repulsive potential); it is of principal importance to note that the SIZ arise not only under interaction of equal defects but, for example, under elastic interaction between the different component interstitials; (5) the interaction of the crystal electron subsystem with the lattice defects being formed.

The general kinetic equation for the interstitial concentration c_i in a single-component lattice is

$$\frac{dc_i}{d\Phi} = \sigma[1 - p_{rec}(\Phi)], \quad (1)$$

where p_{rec} is the recombination probability of the specific defect i with that complementary thereto, i.e., with a vacancy. Let p_{rec} be expressed as the ration of the volume occupied by all RIZ, including the radiation-induced and pre-irradiation ones, to the fraction of the total crystal volume V free of SIZ generated by other defects,

$$p_{rec} = \frac{V_{SIZ}(\Phi)}{V - V_{SIZ}(\Phi)}. \quad (2)$$

Let f_{iv} and f_{ii} denote the dimensionless RIZ and SIZ volumes, respectively; ω_a is the average volume of the lattice atom; N is the number of lattice sites in a specified volume. Then, taking into account the concentration of pre-irradiation vacancies and that of the interstitial of a specific kind, we have

$$V_{SIZ}(\Phi) = f_{iv}N[c_{0v} + c_v(\Phi)]\omega_a$$

$$V_{RIZ}(\Phi) = f_{iu}N[c_{0i}] + c_i(\Phi)\omega_a ,$$

$$V = N\omega_a. \tag{3}$$

The kinetic equation is written as

$$\frac{dc_i}{d\Phi} = \sigma \left[1 - \frac{f_{iv}(c_{0v} + c_v)}{1 - f_{iu}(c_{0i} + c_i)} \right]. \tag{4}$$

In (4), both possible pre-irradiation defects are taken into account, i.e., vacancies and interstitials. This equation generalizes the expressions given in [13, 14].

In the case of two-component lattice, not only interaction between interstitials of the same sublattice is to be taken into account but also the mutual repulsion of different interstitials as well as all the pre-irradiation defects in both sublattices. Bearing in mind that, according to the above assumptions, the numbers of radiation-induced *i* and *v* for each component are the same, we obtain a system of kinetic equations to determine the interstitial concentrations of both components, *c*₁ and *c*₂:

$$\frac{dc_1}{d\Phi} = \sigma_1 \left[1 - \frac{f_{11}'(c_{01} + c_1)}{1 - f_{11}(c_{01} + c_1) - f_{12}(c_{02} + c_2)} \right] \tag{5}$$

$$\frac{dc_2}{d\Phi} = \sigma_2 \left[1 - \frac{f_{22}'(c_{02} + c_2)}{1 - f_{22}(c_{02} + c_2) - f_{21}(c_{01} + c_1)} \right]$$

where the index 1 denotes the cation (Zn in our case) and 2, the anion (Se). The primed indices relate to vacancies in the respective sublattices. The double indices denote the RIZ or SIZ resulted from the interaction between corresponding defects. Thus, the dimensionless sizes of the instability zones expressed in terms of the mean atomic volumes in the lattice are as follows: *f*_{11'}, the squeezing zone RIZ volume (*I*_{Zn}⁻*V*_{Zn}); *f*₁₁, the displacement zone SIZ volume (*I*_{Zn}⁻ *I*_{Zn}); *f*_{22'}, the RIZ (*I*_{Se}⁻*V*_{Se}); *f*₂₂, the SIZ (*I*_{Se}⁻ *I*_{Se}); *f*₁₂ = *f*₂₁, the SIZ (*I*_{Zn}⁻ *I*_{Se}, *I*_{Se}⁻ *I*_{Zn}).

Some comments to the system of equations (5) seem to be necessary. It is of course symmetric with respect to the substitution 1 for 2. But attention is to be given that some items are omitted in the right-hand sides of the equations that seem to be obligatory, and just those responsible for the interaction of vacancies with each others as well as those defining the size of instability zones including an interstitial

from one sublattice and a vacancy in another one. Of course these items are easy to introduce into the system (5) to preserve its generality. These items are omitted for two reasons. The *v-v* interactions do not influence the defect accumulation, at least if those are introduced in an uniform manner, since the vacancy migration energy is so high that neither RIZ nor SIZ of a size exceeding interatomic spacings are formed, thus, the cross-sections of processes associated with such interactions are several orders smaller than those taken into account in (5). The interactions of interstitials from one sublattice with vacancies from another one seem to have the cross-sections of the order of the RIZ size. Nevertheless, those do not contribute essentially to the accumulation kinetics of radiation defects due to the following causes. The vacancies, having a volume smaller than that of atoms dislodged from their lattice sites, generate elastic displacements directed towards the vacancy. In contrast, the interstitials expand the lattice. The elastic interaction between *v* and *i* defines their attraction and the RIZ presence in metals. In non-metallic compounds, the defects are electrically charged, therefore, the vacancies of one sublattice and interstitials of another one have the same sign, thus, repel each other. Generally speaking, the superposition of the elastic potential and electrostatic one may result in stationary states, weakly bound complexes, which are stable only at very low temperatures while at higher ones, those do not influence essentially the accumulation of radiation-induced defects (see [2]). The saturation concentrations, *c*₁ and *c*₂, of the interstitials from both sublattices are defined by the conditions *dc*₁/*dΦ* = *dc*₂/*dΦ* = 0 which are reduced to the solution of the system of linear algebraic equations

$$f_1 \bar{c}_1 + f_1 \bar{c}_2 = \beta_1,$$

$$f_{21} \bar{c}_1 + f_2 \bar{c}_2 = \beta_2, \tag{6}$$

where

$$\beta_1 = 1 - f_{11}'c_{01}' - f_{11}c_{01} - f_{12}c_{02};$$

$$\beta_2 = 1 - f_{22}'c_{02}' - f_{22}c_{02};$$

$$f_1 = f_{11} + f_{11}'; f_2 = f_{22} + f_{22}.$$

*f*₁ and *f*₂ are the total RIZ and SIZ volumes for interstitial from both sublattices. The saturation concentrations in each sublattice are as following

$$\begin{aligned} \bar{c}_1 &= \frac{\beta_1 f_2 - \beta_2 f_{12}}{\Delta}, \\ \bar{c}_2 &= \frac{\beta_2 f_1 - \beta_1 f_{21}}{\Delta}, \end{aligned} \quad (7)$$

where $\Delta = f_1 f_2 - f_{12} f_{21}$.

In the absence of pre-irradiation defects ($c_{01} = c_{01}' = c_{02} = c_{02}' = 0$), i.e., in the absence of the stoichiometry deviations in the binary compounds, the saturation concentrations are:

$$\bar{c}_1^{(0)} = \frac{f_2 - f_{12}}{\Delta}, \quad \bar{c}_2^{(0)} = \frac{f_1 - f_{21}}{\Delta}. \quad (8)$$

The saturation concentrations of defects in the presence of the stoichiometry deviations (7) can be expressed in terms of saturation concentrations (8) corresponding to the absence of the stoichiometry deviations. After several cumbersome but simple transformations, we obtain

$$\bar{c}_1 = \bar{c}_{10} - k_{1\alpha} c_{0\alpha}, \quad \bar{c}_2 = \bar{c}_{20} - k_{2\alpha} c_{0\alpha}, \quad (9)$$

where the index α denotes the defect type (1, 1', 2, 2') and the values of coefficients k are summarized in the Table according to the initial defect type.

It follows from (9) that the saturation concentrations, at least within the frame of the model proposed, depend linearly on the pre-irradiation defect content, in particular, on the stoichiometry deviation, whereas deviations of different types influence in different manner not only the resulting effect value but even may change its sign.

In the case when the pre-irradiation defects of two types, α and γ , are present simultaneously, as is described above, we have

$$\begin{aligned} \bar{c}_1 &= \bar{c}_{10} - (k_{1\alpha} c_{0\alpha} + k_{1\gamma} c_{0\gamma}), \\ \bar{c}_2 &= \bar{c}_{20} - (k_{2\alpha} c_{0\alpha} + k_{2\gamma} c_{0\gamma}). \end{aligned} \quad (10)$$

Let us define the term "material radiation resistance" more precisely. It seems that this property is quite understandable intuitively. Actually, however, very different properties are implied when speaking about the material radiation resistance. If the enormous irradiation doses typical of the nuclear reactor materials are considered, it is of importance to establish the extent of the parameter conservation at doses defining the saturation concentrations. In contrast, if it is a matter of rela-

tively small doses being actual, e.g., in medical applications, the radiation resistance is to be estimated as the parameter change extent at the initial irradiation stages far from the saturation ones. It is easy to see, however, that the radiation resistance characteristics corresponding to very great and very small irradiation doses are in correlation together. In fact, e.g., from (4) we obtain that the concentration variation rate $\kappa = dc_i/d\Phi$ at the limit $\Phi = 0$ is

$$\kappa = \sigma \left[\frac{1 - f_{iv} c_{0i} - f_{iv} c_{0v}}{1 - f_{iv} c_{0i}} \right] \quad (11)$$

the saturation concentration c_{isat} ,

$$c_{isat} = \frac{1 - f_{iv} c_{0v} - f_{iv} c_{0i}}{f_{iv} + f_{iu}}, \quad (12)$$

and the ratio κ/c_{isat} ,

$$\frac{\kappa}{c_{isat}} = \sigma \frac{f_{iv} + f_{iu}}{1 - f_{iv} c_{0i}}, \quad (13)$$

therefore, when determining the saturation concentrations, it is possible to determine also the resistance extent also under small doses:

$$\kappa = \sigma c_{isat} \frac{f_{iv} + f_{iu}}{1 - f_{iv} c_{0i}}. \quad (14)$$

3. Instability zones, the defect charge states and the radiation resistance of binary semiconductors

In the Paragraph 1, the physical causes of the RIZ and SIZ formation for point defects in crystals have been considered. Their sizes can be expressed quantitatively for different defect interaction potentials according to [2]. At the electrostatic interaction between the point defects, the absolute instability radius for the IZ of interstitials near a vacancy is

$$r^{es} = Ze(a/\epsilon U_m)^{1/2} \quad (15)$$

both for the RIZ and SIZ while at the elastic interaction,

$$r^{el} = (3Ga\Delta V_1 \Delta V_2 / U_m)^{1/4}, \quad (16)$$

where a is the interatomic spacing; U_m , the migration energy of the interstitial; ϵ , dielectric constant; e , the electron charge; Ze ,

the defect charge; G , shear module; ΔV_1 and ΔV_2 , the differences between the volumes of regular positions in the crystal and those of defects localized in those positions.

What are the instability zones, i.e., electrostatic or elastic ones, that define the fast recombination and mutual squeezing the defects? For metals, the picture is obvious. In this case, the RIZ and SIZ are defined by elastic interaction only and are described by (16), and it is just the atomic radii of interstitials that define the corresponding ΔV_1 and ΔV_2 . In crystals having the interatomic bindings are similar to pure ionic ones, the maximum IZ size is obvious to be defined by the Coulomb interaction and thus by the expression (15). The most general case of non-metallic crystals includes the semiconductor compounds where the chemical binding is a superposition of two quantum states of electrons. The one state is defined by the wave function describing the covalent binding while the other, by that describing to the pure ionic one. The ionicity extent is the measure of each state contribution to the total wave function. Using the Landau-Ziner theorem, it can be shown that even if the ionicity degree is very low, the atoms take the charged (ionic) state after the binding breaking due to an external attack at a probability close to 1, to the kinetic energy received by the atom moving away is high enough [2].

This seems to mean that both RIZ and SIZ must be defined by the Coulomb interaction and the Eq.(15) in ionic crystals as well as in ionic-covalent ones, since the electrostatic IZ exceed in size considerably the elastic ones. Meanwhile, it may appear that the electrostatic interaction of the radiation-induced lattice defects will not be manifested in semiconductors at all. In fact, not only vacancies and interstitials are formed under ionizing irradiation but also free charge carriers, electrons and holes. The local concentration of those carriers is particularly high just in the region where

the radiation-induced defect is generated, since the braking of the released particle, in particular, of an ion, is defined mainly by the energy exchange accompanied by the electron subsystem excitation.

Let us estimate characteristic relaxation time for electrons and holes, on the hand hand, and of ions, on the other one, resulting in the neutralization of the latter. For electron, the mean free path is $\lambda = 1/n\sigma$ and its mean lifetime with respect to the recombination with an opposite-charged ion is $\tau = \lambda/v = (nv\sigma)^{-1}$ where n is the number of electrons (or holes) per unit volume; v , their mean thermal speed, $v = (3kT/m)^{1/2}$; T , the temperature; k , the Boltzmann constant; m , the electron (or hole) effective mass. Assuming the cross-section σ is defined by the Onsager radius $r = Ze^2/kT$ where Ze is the ion charge and e , the electron charge, we obtain

$$\sigma = m^{1/2}(kT)^{3/2} e^{-4} n^{-1} z^{-2}. \quad (17)$$

What is the capturing probability of a free charge carrier by a radiation-originated ion when the ion recombination time with a vacancy within the RIZ does not exceed 10^{-10} s (see [2])? The local charge carrier concentration sufficient for a charged lattice defect would able to capture an electron (or hole) prior to recombination of the complementary lattice defects is as low as 10^{16} cm³, that is obviously lower that the concentration of electrons and holes in the region where the radiation-induced defect is arisen. In this case, the electrostatic RIZ are not manifested at all.

The conclusion drawn from these estimations is of a primary importance for the forecasting and interpretation of the radiation effects on semiconductor crystals. It appears that the radiation-induced lattice defects, being charged right from their birth, may interact with each other as neutral ones, since the ion-electron neutralization proceeds so fast that the heavy ions have no time to "think what they have to

Table

Pre-irradiation defect type	α	$k_{1\alpha}$	$k_{2\alpha}$	$K_{1\alpha}(\text{ZnSe})$	$K_{2\alpha}(\text{ZnSe})$
Zn	1	$1-f_{11}f_2/\Delta$	$f_{21}f_{11}/\Delta$	0.7	0.2
V_{Zn}	1'	$f_{11}f_2/\Delta$	$-f_{11}f_{21}/\Delta$	0.3	-0.2
I_{Se}	2	$f_{12}f_{22}/\Delta$	$1-f_{22}f_1/\Delta$	0.8	0.15
V_{Se}	2'	$-f_{22}f_{12}/\Delta$	$f_{22}f_1/\Delta$	-0.8	0.9

do". The electrostatic interaction between the initially charged radiation-induced defects disappears and the situation is defined by the elastic interactions.

As to the elastic displacement in the vicinity of vacancies, the atoms surrounding the vacancy are shifted towards the latter as a rule. The characteristic shift values are about 0.1 to 0.2 Å. The interstitials always expand the lattice, thus, the surrounding atoms become shifted away from those. To estimate the RIZ and SIZ size using (15) or (16), it is necessary to establish what crystal-chemical radii of interstitials arisen due to the radiation action define effectively the RIZ and SIZ and at final count, according to (9), (10) and (14), the radiation resistance of the two-component semiconductor.

As an example of the general consideration, the binary semiconductor ZnSe will be taken to study the possible mechanisms of the point defect interaction. In the numerical estimations, the migration energy of the intrinsic interstitials is assumed to be 0.1 eV (see [2]).

If the RIZ and SIZ are defined by the electrostatic interaction, then, as follows from (15), for double-charged defects r^{es} is 23 Å and the number of positions in the IZ is about 10^3 . If, as is described above, the radiation-induced ions and vacancies become neutralized prior to recombination, then the IZ are defined by the elastic interaction with much smaller sizes (16).

Taking ZnSe as an example, let the problem be discussed: what crystal-chemical radii define the elastic IZ. The knocked off double-charged zinc ion may trap the missing electrons into its free orbitals; in this case, its crystal-chemical size in the defect interaction estimation is close to the atomic radius. Another type of the electron capturing is possible, not into the zinc atomic orbitals but into energy levels within the semiconductor band gap. These levels are deep ones characterized by small localization regions of about two or three Angstrom units, thus obviously less than r^{es} . In this case, the Coulomb potential of the interstitial zinc is not manifested but its crystal-chemical radius defining the elastic defect interaction is just the ionic (not atomic) one. The lattice relaxation time near the defect is defined by the Debye frequency (10^{12} to 10^{13}). Comparing it to the minimum recombination time of complementary defects (10^{-11} s) and with their neutralization time (10^{-13} s), it may be con-

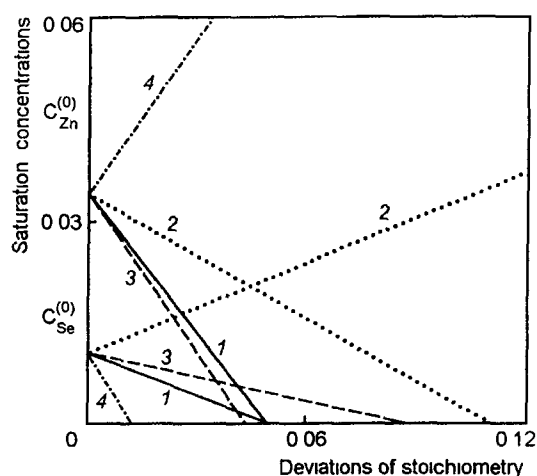


Fig. 1. The saturation concentrations as functions of the stoichiometry deviations according to (9), ZnSe is taken as an example. 1, 3 — interstitial Zn and Se, respectively; 2, 4 — Zn and Se vacancies, respectively. The saturation concentrations of zinc and selenium defects in stoichiometric crystal are assumed to be $3.4 \cdot 10^{-2}$ and $1.1 \cdot 10^{-2}$, respectively.

cluded that the local charge equilibrium is established most probably prior to the lattice one, therefore, the crystal-chemical radius of zinc interstitials defining the elastic interactions answers just by the zinc ion size. (The lattice polarization energy is neglected but it is obvious that its taking into account will enhance the predominance of ionic radii in the elastic energy estimations).

As to selenium interstitials, the ionic radius of the double-charged negative selenium ion is so large that the elastic deformation energy exceeds any possible gain due to the lattice polarization. The ionization potential of the excess electrons of the negative Se ion is small as compared to that of neutral atom. At a large interaction cross-section of the dislodged ion with the lattice atoms, this fact predetermines a high probability of the excess electron loss. The atomic radius of Se is considerably smaller than the ionic one, therefore, the radiation-originated Se ions become most probably neutralized losing the excess electrons (that is equivalent to the hole capturing) and are transformed into the atomic state. Thus, it is most likely that the radiation-induced zinc ions become neutralized due to the electron capturing into deep acceptor levels within the semiconductor band gap and it is just the ionic radii that define their elastic interaction with other defects;

while the radiation-originated negative selenium ions become transformed into neutral atoms. The radii of elastic RIZ and SIZ calculated according to (16) using the data on the ionic and atomic radii in crystals [13] and the structure void sizes in the lattice determined geometrically basing on the closest packing theory (see [2]) turn out to be within limits of 3 to 7 Å.

The parameters of Eq.(9) for ZnSe are given in two last columns of the table 1. Fig. 1 presents the saturation concentrations of zinc and selenium interstitials vs. the stoichiometry deviation values, i.e., the concentrations of different types of pre-irradiation defects (see the Figure caption).

It follows from the Eq.(9) and the Figure that the saturation concentrations of defects in different sublattices may both increase and decrease, depending on the character of the stoichiometry deviation. In particular, if the stoichiometry deviations are defined by the vacancies in the selenium sublattice, then this results in a sharp drop of the saturation concentration in the selenium sublattice but at the same time, the saturation concentration in the zinc sublattice increases. The defect saturation level in the zinc sublattice decreases due to the effect of pre-irradiation vacancies in the zinc sublattice; however, the same effect results in an increase of the saturation concentration in the selenium sublattice. If the stoichiometry deviation consists in the formation of interstitials, the saturation concentrations in both sublattices become decreased as compared to those in the stoichiometric crystal. It is just the universality of SIZ that defines this universal effect of the pre-irradiation interstitials, since the elastic repulsion of defects is obviously independent of the interstitial kind involved in the interaction. The conclusion is that to provide an increased radiation resistance of the binary semiconductors, such ones care to be searched for where the equilibrium stoichiometry deviations are defined by the inserted interstitials. The latter favor more effectively the defect recombination. According to (10), the crystalline compounds where the stoichiometry deviations are defined both by the interstitials and vacancies are also of good prospects with respect to the radiation resistance (see [5, 6]).

On the other hand, the consideration of the kinetic equations presented above and expressions (15), (16) allows to draw some conclusions about the defect charge states.

In fact, the known Watkins paradox [14] consisting in that only interstitial zinc is revealed in irradiated ZnSe while there are no defects in the selenium sublattice can be interpreted in a quite definite manner. It is unexpected in fact, since the interstitial zinc is more mobile (has a lower migration energy) and it seems that it should annihilate prior to other defects. What is the matter? It is most likely that the crystals used in experiments [14] exhibited the stoichiometry deviations towards the zinc excess and vacancies were formed in the selenium sublattice. It is shown in the Fig. 1 that in this case the selenium defects disappear at a higher rate while the zinc interstitials are accumulated. This is possible, however, if the zinc RIZ are defined only by elastic interactions, since otherwise the Coulomb RIZ having a volume exceeding at least one decimal order that of the elastic ones, would result, in first turn, in the recombination of zinc defects. The Watkins data demonstrate that the defects, although charged at the origination, become neutral prior to annihilation. The analysis of the irradiation effects using the model (5) makes it possible to diagnose the charge states of defects.

Conclusions

1. The system of differential equations has been proposed to describe the accumulation kinetics of radiation-induced defects taking into account both attraction and repulsion potentials.

2. The absolute instability zones of complementary defects defining their recombination as well as the zones of absolute squeezing of defects similar in the electric charge sign or in the elastic displacement direction have been shown to effect to the equivalent extent the material radiation resistance, thus allowing to interpret the anomalous large sizes of the defect instability zones in metals.

3. The stoichiometry deviations defining the presence of pre-irradiation defects in multicomponent crystals have been shown to influence substantially the material radiation resistance both under small and large irradiation doses, thus providing the possibility for a priori selection of improved radiation-resistant materials as well as the stoichiometric preconditions of the radiation stability improvement.

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Взаємодія дефектів та радіаційні властивості багатокomпонентних напівпровідників

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Розглянуто вплив зон абсолютної рекомбінації та абсолютного витіснення взаємодіючих дефектів ґратки. Показано, що відштовхування дефектів, так само як їх притягання, призводить як до зменшення асимптотичної концентрації радіаційних дефектів при великих дозах опромінення, так і до зростання радіаційної стійкості матеріалів при малих дозах. Аналіз показує, що відхилення від стехіометрії у двокомпонентних кристалах значно впливають на радіаційну стійкість, а добір термодинамічних параметрів синтезу кристалів дозволяє регулювати кількість радіаційних дефектів, в тому числі забезпечувати можливість підвищення радіаційної стійкості стосовно дефектів в обох підґратках.