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INSTABILITIES IN BINARY COMPOUNDS UNDER IRRADIATION

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A simulation of radiation-induced instability in binary semiconductors, such as GaAs, was fulfilled. The instability is connected with antisite defects accumulated. It was shown that the number of antisite defects in crystal under irradiation can significantly exceed their equilibrium concentration. We have found that the instability with respect to periodical defect distribution appears at some conditions of irradiation. The wavelength of the periodical distribution was estimated as 100 nm - 10 μm depending on crystal parameters.Introduction

Radiation is an effective tool for studying properties of materials. In multicomponent systems radiation can cause transitions to new phases (see review [1]). Because irradiated substances are far from equilibrium, effects of self-organization can be found in these systems [2]. For instance, the periodical distribution of point defects can appear even in the case of uniform radiation and uniform sink density.

Spatial modulation of composition of different materials was observed experimentally in many works [3 - 5]. For instance, in [3, 4] the oscillations of the composition of Fe-Ni and Fe-Ni-Cr alloys were detected after irradiation by Ni^{+} ions with the energies of 5 MeV.

This effect has been investigated earlier for simple substances ([6, 7]). The possibility of oscillation appearance is discussed in [8]. In [9] we predicted this phenomenon for ordered multicomponent alloys. In this work we analyze such an effect in binary semiconductors.

First, we shall calculate the stationary values of defect concentration assuming uniform defect distribution. Then we shall perform the stability analysis of such distribution.

1 Defect concentrations in the case of uniform distribution

Let us consider how the radiation influences materials. A binary compound consists of two types of atoms, which we denote as A and B. In a fully ordered compound each type of atom forms the sublattice (Fig. 1,a). Even in the absence of radiation, there is a great number of point defects in the crystal. The typical defects for ordered multicomponent compounds are antisite defects, i.e. atoms that occupy the wrong sublattice (Fig. 1b). The radiation knocks the atoms of both types out of their sites, creating interstitial atoms and vacancies. Then these point defects diffuse over the crystal and participate in different reactions. For example, an interstitial atom and a vacancy can recombine mutually. After recombination of interstitial atom and vacancy of the same type the ideal crystal is restored. But if their types are different, the antisite defect appears (Fig. 1c). Unlike the interstitial atoms and the vacancies, the antisite defects migrate very slowly and they are accumulated in the crystal. In thin samples radiation creates defects almost uniformly. This is true for neutron and electron irradiation, which can penetrate deep into the sample. So we assumed that the distributions of defects are also uniform. Defect concentrations can be determined with the reaction rate method. We considered the following point defects: interstitial atoms of both types (their concentrations we denoted as I_A and I_B), vacancies on both sites (V_a and V_b) and antisite defects (A_b and B_a). We used dimensionless units for concentrations, in which the volume of one crystal unit cell is equal to 1.

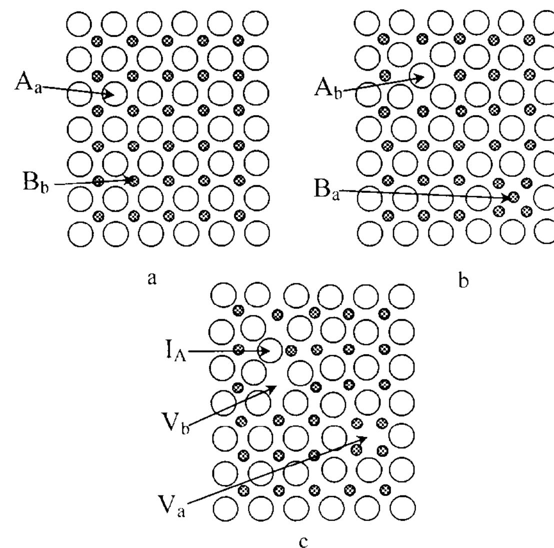

Fig. I, a - ordered binary compound; b - antisite defects; c - recombination ofla and Vb that leads to creation of the antisite defect

Time dependence of radiation defect concentrations is determined by the following kinetic equations:

$$\frac{dI_A}{dt} = K_{ai}^{A} A_a - K_{ia}^{A} I_A V_a - K_{ib}^{A} I_A V_b + K_{bi}^{A} A_b - K_{ib}^{AB} I_A B_b + K_{ib}^{BA} I_B A_b + K_{ia}^{BA} I_B A_a - K_{ia}^{AB} I_A B_a - \alpha_{IA} (I_A - nI_A) + K_0 [A_a + A_b - z (V_a + V_b)/2]; \quad (1)$$

$$\frac{dV_a}{dt} = K_{ai}^{A} A_a - K_{ia}^{A} I_A V_a - K_{ia}^{B} I_B V_a + K_{ai}^{B} B_a - K_{ba}^{B} V_a B_b + K_{ab}^{B} V_b B_a + K_{ab}^{A} V_b A_a - K_{ba}^{A} V_a A_b - \alpha_{Va} (V_a - nV_a) + K_0 (1 - z V_a) (A_a + B_a); \quad (2)$$

$$\frac{dA_b}{dt} = K_{ib}^{A} I_A V_b - K_{bi}^{A} A_b + K_{ib}^{AB} I_A B_b - K_{ib}^{BA} A_b I_B +$$
$$+ K_{ab}^{A} V_b A_a - K_{ba}^{A} V_a A_b - \alpha_{IA} (I_A - nI_A) A_b / 2 +$$
$$+ \alpha_{IB}(I_B - nI_B) B_b/2 + \alpha_{Va}(V_a - nV_a)/2 -$$
$$- K_0(A_b - zV_b). \qquad (3)$$

The remaining three equations for I_B, V_b and B_a can be written analogously after changing A↔B and a↔b. The equations for A_a and B_b can be obtained from the conservation of site numbers: $A_a + B_a + V_a = 1$ and $B_b + A_b + V_b = 1$.

The following defect reactions were included in these equations:

1) recombination of interstitial atoms with the same or different types of vacancies (i.e. reactions like $I_A + V_b \rightarrow A_b$ or $I_A + V_a \rightarrow A_a$);

2) thermal creation of Frenkel pairs from antisite defects and from atoms localized on their own sites (i.e. $A_b \rightarrow I_A + V_b$ and $A_a \rightarrow I_A + V_a$);

3) substitution of atoms or antisite defects with interstitial atoms (e.g. $I_A + B_a \leftrightarrow A_a + I_B$);

4) atom transition to the vacancy in the other sublattice with ordering or disordering (e.g. $A_b + V_a \leftrightarrow A_a + V_b$);

5) capture of interstitial atoms and vacancies by unsaturable sinks, such as dislocations and surface (terms with α; nI_A, nI_B, nV_a, nV_b are the thermal concentrations of corresponding defects);

6) creation of Frenkel pairs by radiation (terms with K_0; the terms containing z take into account the dynamic recombination of interstitials and vacancies, where z is the number of atoms in the region of dynamic recombination [10]).

Coefficients K can be evaluated from diffusion parameters. Some of them are related by the detailed balance principle. In this work we assumed that defect energies and diffusion barriers do not depend on the order parameter. So, we restricted ourselves to low concentration of antisite defects, i.e. up to several percent.

There are a lot of parameters needed to obtain all coefficients. Most of them have been determined experimentally using different techniques (see [11]). But exact values for some parameters are still unknown. For example, determination of energy barriers for vacancy jumps is very difficult due to variety of mechanisms existing in binary semiconductors. In this work we used the parameter values determined for GaAs.

To estimate the stationary values of defect concentrations, we set time derivatives in kinetic equations to zero and solved the set of eight algebraic equations. Four of them turn out to be linear and the others are quadratic. This set was reduced analytically to that of two equations, both of ninth order. Further solving was performed numerically. It is necessary to be extremely careful while performing numerical calculations in such systems. Terms in these equations can be of different orders and computational errors can be significant. To avoid this, we worked with high precision numbers using software from [12].

The temperature dependences of these stationary values at defect production rate $K_0 = 10^{-5}$ dpa/s are presented in Fig. 2.

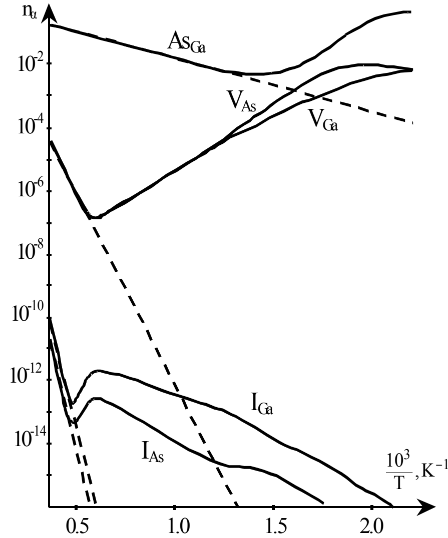

Figure 2: Dependence of point defect concentration on temperature at defect production rate = 10^{-5} dpa/s. The scale on the x axis is proportional to the inverse temperature

Dashed lines represent the defect concentration in the absence of radiation. The minimum in vacancy and antisite defect concentration is caused by competition of two mechanisms of defect creation. At high temperatures the thermal fluctuations determine thes defect concentrations. At low temperatures the defect concentrations are determined by the rates of radiation defect creation and thermally activated annealing. From Figure 2 it is seen that the antisite defect concentration is large, particularly at low temperatures of the environment.

DEVELOPMENT OF PERIODICAL STRUCTURES

Now we should check the stability of the uniform defect distribution obtained above. Let us consider qualitatively why the uniform distribution can be unstable. The lattice gets deformed around the antisite defects due to the different size of atoms. This field of deformation affects migration of interstitial atoms and vacancies to antisite defects, hence, the processes of their recombination. If interstitial atoms are attracted to the regions of higher concentration of antisite defects, then they recombine mostly there. This leads to further increase of antisite defect density in these regions and to its decrease in other regions. As a result, the defect distribution function becomes periodic in space. Such type of distribution is a superlattice of defect density.

To analyze this phenomenon quantitatively the kinetic equations were modified to include diffusion terms, which appear in non-homogeneous fields. Let us consider the diffusion of the interstitial atoms of type A as an example. The migration of interstitial atoms can

be described with a reaction $I_A(\mathbf{r}) \leftrightarrow I_A(\mathbf{r} + \mathbf{dr})$, where **dr** is the vector connecting two neighbor interstitial positions. We took into account that both concentration and energy of interstitial atoms are functions of coordinates. As a result the following term was added to the time derivative of interstitial atom concentrations:

$$\left(\frac{\partial I_A(r)}{\partial t}\right)_{diff} = \mathrm{div}\left[D_{IA}\cdot\left(\nabla I_A(\mathbf{r}) + I_A(\mathbf{r})\frac{\nabla U_{IA}(\mathbf{r})}{kT}\right)\right] \tag{4}$$

Index "diff" means that we wrote here only the terms describing the diffusion of interstitial atoms, ∇ is the gradient operator. $U_{IA}(\mathbf{r})$ is the external potential that describes the interaction of point defects. In this work only interaction with antisite defects was taken into account, because their concentrations are larger than those of other defects. Thus the potential for interstitial atoms of type A was written as

$$U_{IA}(\mathbf{r}) = \int\left[U_{Ab,IA}(\mathbf{r}-\mathbf{r}')\cdot A_b(\mathbf{r}') + U_{Ba,IA}(\mathbf{r}-\mathbf{r}')\cdot B_a(\mathbf{r}')\right] dV' \tag{5}$$

$U_{Ab,IA}(\mathbf{r} - \mathbf{r}')$ is the interaction energy of the antisite defect A_b situated in $\mathbf{r}$ and the interstitial atom I_A in $\mathbf{r}'$. It is seen that if defect concentrations are uniform, then $U_{IA}(\mathbf{r})$ is constant and both gradients in (4) are equal to 0.

For defect-defect interaction the following equation was used [13]:

$$U_{\alpha,\beta}(\mathbf{r}) = \frac{3\Delta V_\alpha \Delta V_\beta}{8\pi r^3}\left(\frac{K}{C_{11}}\right)^2 (-C_a)\left[3 - 5\left(\cos^4\theta_x + \cos^4\theta_y + \cos^4\theta_z\right)\right], \tag{6}$$

where C_a is the anisotropy parameter, which is negative for most of crystals. C_{11}, K are the elastic constants, θ_i is the angle between the radius vector **r** and i-th crystal axis, ΔV is the parameter that characterizes the volume change due to introduction of the defect. In the case of cubic crystals with weak anisotropy, when the distance between the defects is much larger than the lattice period, this formula describes the defect-defect interaction. If the radius vector connecting the defects is oriented along the crystal axis, the defects of the same type attract each other.

The values of the elastic constants for GaAs were taken from [14]. Calculations of ΔV for GaAs were made in [15] using *ab initio* simulations.

The diffusion of other interstitial atoms and vacancies can be described in a similar way. Also all reactions in equations (1) - (3) have additional terms in the non-homogeneous case.

Now we can check the stability of the uniform defect distribution. To do this, we represent all the concentrations as stationary uniform values and small non-uniform deviations around those values. For example, the concentration of the antisite defects A_b was written as

$$A_b = A_{b0} + \delta A_b \exp(i\mathbf{kr} + \lambda t) \tag{7}$$

where A_{b0} is the uniform stationary value obtained earlier in this work. All other concentrations were written in such a form also. Then we substituted them in the equations (1) - (3) modified to non-uniform distributions. After substitution of (7) into (5) we obtained Fourier transform of the defect-defect interaction potential (6). It has the following form:

$$U_{\alpha,\beta}(\mathbf{k}) = \left(\frac{K}{C_{11}}\right)^2 (-C_a)\,\Delta V_\alpha\,\Delta V_\beta\,\frac{k_x^4 + k_y^4 + k_z^4}{k^4}$$

8)

One can see from this formula that interaction is maximum if the wavevector is directed along the crystal axis.

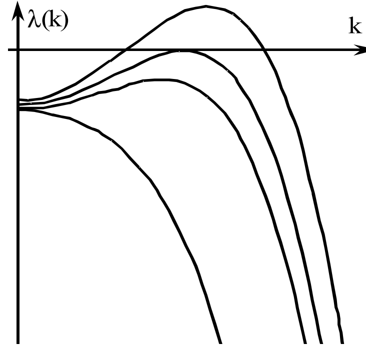

*Fig. 3. The typical λ(**k**) for different irradiation intensities and temperatures*

Because we needed only to check the stability of roots, we assumed that the deviations are small. Keeping only the linear terms in deviations, we obtained a system of linear equations. This system has a nontrivial solution if its determinant is zero, which enabled us to determine $\lambda(\mathbf{k})$. The stationary solution is stable if and only if real parts of all $\lambda(\mathbf{k})$ values are negative.

The typical $\lambda(\mathbf{k})$ for different irradiation intensities and temperatures are shown in Figure 3. When defect concentrations are small and the interaction is not significant, $\lambda(\mathbf{k})$ is negative and the absolute value of λ is higher for large values of k. It is seen as the effect of diffusion, which suppresses the non-uniform fluctuations. When defect concentration increases, the interaction becomes more important. Some fluctuation obtains positive feedback, i.e. Re $\lambda(\mathbf{k})$ takes positive values in some region of **k** values. It means that small fluctuations with such **k** grow, which leads to the development of the superlattice. The absolute value of **k** gives us the period of the superlattice. Results of stability analysis of the uniform solutions are presented in the plane of irradiation intensity (K, dpa/s) and environment temperature (T_0) (see Figure 4). In the region 1 the uniform values of defect concentrations are stable. In the region 2 the system becomes unstable, which leads to the development of the superlattice. It should be noted that in the cubic crystals the instability appears simultaneously for several states with different

values of **k**, which have the same modulus but different directions. As the result complex structures like Bйnard cells may develop. The typical period of the superstructures depends on the crystal and external parameters and varies from 10^2 to 10^5 lattice periods. It is possible to vary the period of the superstructure by changing the intensity and temperature of irradiation.

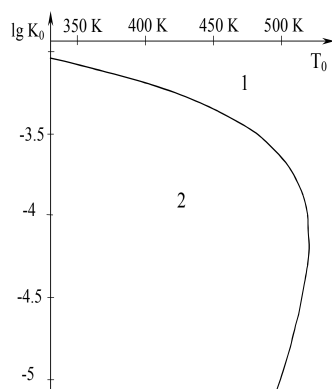

Fig. 4. Regions of instabilities on the plane of irradiation intensity and environment temperature

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