
SEMICONDUCTOR STRUCTURES, LOW-DIMENSIONAL SYSTEMS, AND QUANTUM PHENOMENA

Effect of Bi Isovalent Dopants on the Formation of Homogeneous Coherently Strained InAs Quantum Dots in GaAs Matrices

R. M. Peleshchak^a, S. K. Guba^{b^}, O. V. Kuzyk^a, I. V. Kurilo^b, and O. O. Dankiv^a

^a Franko State Pedagogical University, Drohobych, 82100 Ukraine

^b Lviv National Polytechnic University, Lviv, 79013 Ukraine

[^]e-mail: gubask@polynet.lviv.ua

Submitted January 30, 2012; accepted for publication June 6, 2012

Abstract—The distribution of hydrostatic strains in Bi³⁺-doped InAs quantum dots embedded in a GaAs matrix are calculated in the context of the deformation-potential model. The dependences of strains in the material of spherical InAs quantum dots with substitutional (Bi → As) and interstitial (Bi) impurities on the quantum-dot size are derived. The qualitative correlation of the model with the experiment is discussed. The data on the effect of doping on the morphology of self-assembled InAs:Bi quantum dots in a GaAs matrix are obtained.

DOI: 10.1134/S1063782613030196

1. INTRODUCTION

In recent years, a new approach to controlling the properties of semiconductor quantum-dot (QD) heterostructures has been developed. The approach is based on the introduction of a single impurity atom into a QD [1]. This problem is prospective for present-day optoelectronics, specifically, for the production of single-electron devices that may find application in quantum computers [2]. Progress in the development of nanotechnology and the physics of nanostructures has led to the practical implementation of various types of optoelectronic devices based on InAs QD arrays on wide-gap GaAs substrates [3–6]. One of the ways of forming ordered QD arrays is via the self-assembly of QDs on the crystal surface. The kinetics of epitaxial growth and the distribution of strains in the QD–matrix system influence the QD size, shape, and arrangement in the matrix [6–8]. The extraordinary properties of QD structures reveal themselves, only if the QDs are as uniform in size and shape as possible and the QD array is of high density (about 10¹¹ cm^{−2}). Therefore, the main problem in growing QDs is to control their morphology: the average size, density, uniformity, etc. All of these QD characteristics can be controlled by varying the technological parameters of the growth process [9–11]. Another approach to controlling the properties of QD semiconductor heterostructures is based on the introduction of a single impurity atom into a QD [1, 2]. Isovalent doping of single-crystal materials is an important technique for solving many practical problems. One of them these is the removal of uncontrollable impurities from III–V compounds with the Bi isovalent impurity [12, 13]. In this context, it is of importance to gain a deeper understanding of the mechanism for the formation of InAs

QD arrays upon isovalent doping with Bi during growth and to produce highly homogeneous QDs. For this reason, a topical problem is the development of an analytical model of a strained InAs QD containing an isovalent impurity. This model must describe the following physical phenomena:

- (i) the effect of the strain-induced diffusion of adsorbed atoms on the QD size and shape;
- (ii) the interactions of the field of local strains with the InAs QD array during its formation and the effect of these interactions on the QD size, shape, and arrangement in the matrix.

Thus, the purpose of this study is to describe the effect of the Bi isovalent impurity in an InAs QD on the formation and morphology of InAs QDs in the InAs/GaAs system in the context of the deformation-potential model. In this paper, we report the results of studying an InAs/GaAs nanoheterosystem containing spherically symmetric strained InAs QDs with a Bi isovalent impurity.

2. MODEL OF A STRAINED QD WITH AN IMPURITY

The formation of strained QDs in a strained nanoheterosystem by the Stranski–Krastanov mechanism [14] occurs in two stages. In the first stage, a strained pseudomorphous InAs layer grows. As the layer reaches a critical thickness of 1.5–1.7 monolayers (MLs), the second stage begins: the pseudomorphous InAs layer is spontaneously decomposed into a system of crystalline QD islands and an InAs wetting layer with a thickness of about 1 ML [15]. Such decomposition is induced by the relaxation of elastic strains pro-

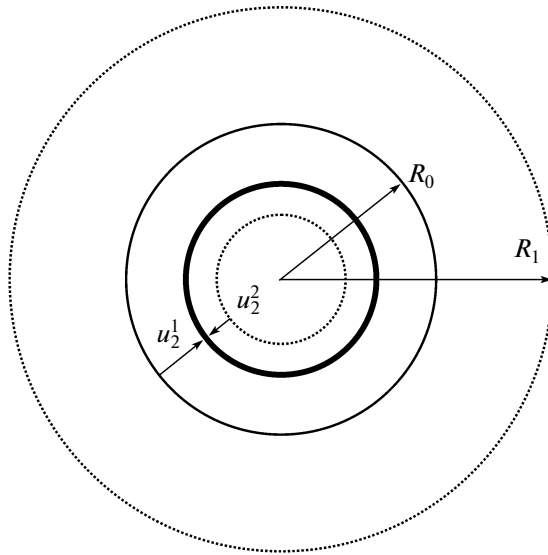


Fig. 1. The model of a strained spherical QD.

duced in the heteroepitaxial system with a lattice mismatch

$$f = \frac{a^{\text{InAs}} - a^{\text{GaAs}}}{a^{\text{InAs}}} \approx 7\%$$

and with different coefficients of thermal expansion for the GaAs substrate and the InAs epitaxial layer ($\alpha_t^{\text{InAs}} = 4.5 \times 10^{-6} \text{ K}^{-1}$, $\alpha_t^{\text{GaAs}} = 5.9 \times 10^{-6} \text{ K}^{-1}$ [16]). The maximal decrease in the free energy of the system is reached at a certain (pyramidal) shape and certain dimensions of the emerging three-dimensional (3D) QD islands. In real systems, the shape and size of individual QDs deviate from the corresponding equilibrium parameters because of nonuniform strains produced in the heterosystem.

In the system of strained islands, there exist two sources of the elastic-strain fields: on the one hand, there is a lattice mismatch between the QD and substrate materials and, on the other hand, there is a step in the surface-tension tensor at the island edges. Correspondingly, the elastic energy is equal to the sum of the energy of elastic relaxation in the bulk, the energy of elastic relaxation at the island edges, and the energy of interaction of the two elastic fields [17].

In this study, we consider QDs that do not exhibit any well-pronounced crystallographic faceting. Specifically, we consider QDs, whose shape corresponds to almost spherical symmetry. For example, in the InAs/GaAs(001) heterosystem, such QDs are formed at thicknesses of the growing InAs layer of about 2 ML [15, 18]. Therefore, in what follows, the contribution of the island edges to the energy of elastic relaxation is disregarded.

In order to reduce the problem for a large number of QDs to that for one QD, we use the following

approximation: the energy of pairwise interaction between QDs is replaced by the energy of interaction of each QD with the averaged (effective) field of elastic stresses σ_{eff} of all other QDs.

The lattice constant of the InAs material to be grown ($a_1 = 6.08 \text{ \AA}$ [19]) is larger than that of the GaAs matrix ($a_2 = 5.65 \text{ \AA}$ [19]). For this reason, upon epitaxial growth of the InAs material on the GaAs layer within the limits of pseudomorphic growth, the InAs material experiences a compressive strain, whereas the GaAs layer experiences a stretching strain. Thus, a spherical QD of radius R_0 can be represented as an elastic dilatation microinclusion shaped as a sphere (thin solid line in Fig. 1) and placed into a spherical cavity in the GaAs matrix (dashed line in Fig. 1). The volume of the cavity is smaller than that of the microinclusion by ΔV .

In order to place such a spherical microinclusion into the above-mentioned cavity, it is necessary to compress the microinclusion and to stretch out the surrounding GaAs matrix in radial directions. The result of the simultaneous influence of strains in the contacting nanomaterials (thick solid line in Fig. 1) can be described by the change in the volume ΔV in terms of the parameter f [20]:

$$\Delta V = f 4\pi R_0^3. \quad (1)$$

Let us consider a spherical QD of radius R_0 embedded into a semiconductor matrix of radius R_1 . Let us assume that an isovalent impurity is located at the center of the sphere.

To determine the strain tensor components $\varepsilon_{ik}^{(i)}$, we must determine the explicit form of the atomic displacements $u_r^{(1)}$ and $u_r^{(2)}$ in the InAs and GaAs materials, respectively. For a QD with an implanted impurity, the equilibrium equation is [20]

$$\begin{aligned} \nabla \operatorname{div} \mathbf{u} &= -D_1 \mathbf{F}^{(1)}(\mathbf{r}), \\ D_1 &= \frac{(1 + \nu_1)(1 - 2\nu_1)}{E_1(1 - \nu_1)}, \\ \mathbf{F}^{(1)} &= \frac{2\Delta\Omega}{3\pi^{3/2}} (C_{11}^{(1)} + 2C_{12}^{(1)}) \frac{1}{r_0^5} r e^{-r^2/r_0^2} \mathbf{n}, \\ \mathbf{n} &= \frac{\mathbf{r}}{|\mathbf{r}|}. \end{aligned} \quad (2)$$

Here, $\mathbf{F}^{(1)}$ is the volumetric force produced by the impurity in the QD; $\Delta\Omega$ is the change in the volume of the QD material due to the embedded isovalent impurity; r_0 is the effective radius of the impurity atom; and ν_i and E_i are, correspondingly, the Poisson coefficients and the Young moduli of the QD material and the surrounding matrix. The parameters ν_i and E_i can be

expressed in terms of the elastic constants $C_{11}^{(i)}$ and $C_{12}^{(i)}$ of these materials in a well-known manner [20].

In the spherical coordinates, the solution of Eq. (2) is

$$u_r^{(1)} = C_1 r + \frac{C_2}{r^2} - \frac{AD_1 r_0^4 e^{-r^2/r_0^2}}{4r} + \frac{AD_1 \sqrt{\pi} r_0^5 \text{Erf}(r/r_0)}{8r^2}, \quad (3)$$

$$0 \leq r \leq R_0,$$

where

$$A = \frac{2\Delta\Omega}{3\pi^{3/2}} (C_{11}^{(1)} + 2C_{12}^{(1)}) \frac{1}{r_0^5}.$$

Since the displacement at the point $r = 0$ must be finite, we must set $C_2 = 0$ in the solution (3).

The atomic displacement in the GaAs matrix is

$$u_r^{(2)} = C_3 r + \frac{C_4}{r^2}, \quad R_0 \leq r \leq R_1.$$

The field of displacements defines the strain tensor components as follows:

$$\varepsilon_{rr}^{(1)} = C_1 + \frac{AD_1 r_0^2 (r^2 + r_0^2) e^{-r^2/r_0^2}}{2r^2} - \frac{AD_1 \sqrt{\pi} r_0^5 \text{Erf}(r/r_0)}{4r^3},$$

$$\varepsilon_{\phi\phi}^{(1)} = \varepsilon_{\theta\theta}^{(1)} = C_1 - \frac{AD_1 r_0^4 e^{-r^2/r_0^2}}{4r^2} + \frac{AD_1 \sqrt{\pi} r_0^5 \text{Erf}(r/r_0)}{8r^3},$$

$$\varepsilon_{rr}^{(2)} = C_3 - \frac{2C_4}{r^3},$$

$$\varepsilon_{\phi\phi}^{(2)} = \varepsilon_{\theta\theta}^{(2)} = C_3 + \frac{C_4}{r^3}.$$

The coefficients C_1 , C_3 , and C_4 can be determined by solving the system of boundary conditions

$$\begin{cases} 4\pi R_0^2 (u_r^{(2)}|_{r=R_0} - u_r^{(1)}|_{r=R_0}) = \Delta V, \\ \sigma_{rr}^{(1)}|_{r=R_0} = \sigma_{rr}^{(2)}|_{r=R_0} - P_L, \quad P_L = \frac{2\gamma\varepsilon^{(1)}}{R_0}, \\ \sigma_{rr}^{(2)}|_{r=R_1} = \sigma_{\text{eff}}. \end{cases} \quad (4)$$

Here, the left-hand side of the first of Eqs. (4) is the geometric difference ΔV between the volume of the microinclusion and that of the cavity in the GaAs matrix (Fig. 1); P_L is the Laplace pressure; and $2\gamma\varepsilon^{(1)}$ is the surface energy of the InAs QD. This surface energy is a function of the surface stress and strain of the QD [21]:

$$\gamma\varepsilon^{(1)} = \gamma(0) + \sum_{i,j} \sigma_{ij}^{(1)} \varepsilon_{ij}^{(1)} + \frac{1}{2} \sum_{i,j,k,l} \varepsilon_{ij}^{(1)} (1) s_{ijkl}^{(1)} \varepsilon_{kl}^{(1)} + \dots$$

Here $\varepsilon_{ij}^{(1)}$ and $\sigma_{ij}^{(1)}$ are, correspondingly, the strain tensor and the surface-stress tensor for the QD and $s_{ijkl}^{(1)}$ is the second-order stress tensor.

The stresses $\sigma_{rr}^{(1)}$ and $\sigma_{rr}^{(2)}$ in the QD and matrix materials are determined as [22]

$$\sigma_{rr}^{(i)} = \frac{E_i}{(1 + \nu_i)(1 - 2\nu_i)} \times [(1 - \nu_i)\varepsilon_{rr}^{(i)} + \nu_i(\varepsilon_{\phi\phi}^{(i)} + \varepsilon_{\theta\theta}^{(i)})]. \quad (5)$$

3. RESULTS AND DISCUSSION

The strain tensor components for the InAs/GaAs nanoheterosystem with strained InAs spherical QDs containing an ionized Bi impurity were calculated with the following parameters [16, 19, 21]:

$$C_{11}^{(1)} = 0.833 \text{ Mbar}, \quad C_{12}^{(1)} = 0.453 \text{ Mbar},$$

$$C_{11}^{(2)} = 1.223 \text{ Mbar}, \quad C_{12}^{(2)} = 0.571 \text{ Mbar};$$

$$D_{001}^{(1)} = 1.088, \quad D_{001}^{(2)} = 0.934;$$

$$\gamma(0) = 0.567 \text{ N m}^{-1}; \quad \sigma_{\text{eff}} = 10^9 \text{ N m}^{-2};$$

$$R_1 = 500 \text{ \AA}.$$

The calculations were performed for two cases: (i) the Bi^{3+} impurity ion substitutes a host As^{3+} ion and (ii) the Bi impurity occupies an interstitial position in the InAs semiconductor material. In case (i), the Bi^{3+} ion radius ($r_0 = 0.12 \text{ nm}$) is larger than the As^{3+} ion radius ($r_{\text{As}} = 0.069 \text{ nm}$), resulting in an increase in the QD volume by $\Delta\Omega = \frac{4}{3}\pi(r_0^3 - r_{\text{As}}^3)$. In case (ii), the

increase in the QD volume is $\Delta\Omega = a_{\text{Bi}}^3$ [23], where $a_{\text{Bi}} = 0.475 \text{ nm}$ is the Bi lattice parameter.

Figures 2 and 3 show the distribution of the hydrostatic strain $\text{Sp } \varepsilon^{(1)}(r)$ in the InAs QD material with the Bi^{3+} impurity which substitutes the host As atom (Fig. 2) or occupies an interstitial position (Fig. 3).

In both cases, the impurity is the center of stretching, and the strain reverses its character in the vicinity of the impurity. With increasing distance from the QD center, the hydrostatic compressive strain of the QD material steadily increases to a value that is virtually no different from that of the impurity-free QD material, in which the compressive strain is caused by the lattice mismatch between the contacting materials. In case (i), the stretching strain produced in the vicinity of the impurity is higher in magnitude and more localized around the QD center. This is attributed to the much smaller effective range of elastic action of a substitutional defect in comparison to that of an interstitial atom ($r_0 - r_{\text{As}} \ll a_{\text{Bi}}$).

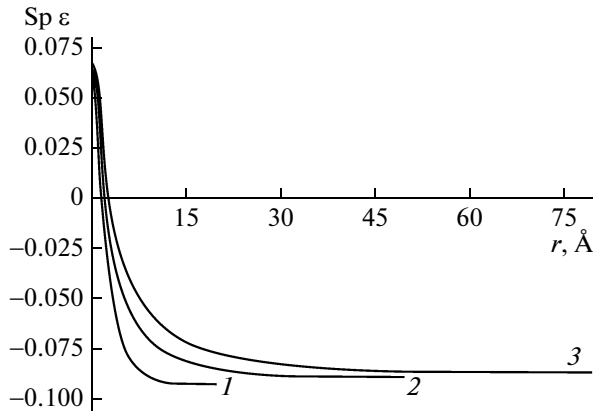


Fig. 2. Hydrostatic strain of the InAs QD material with a substitutional Bi^{3+} impurity for different QD radii: $R_0 =$ (1) 2, (2) 5 and (3) 8 nm.

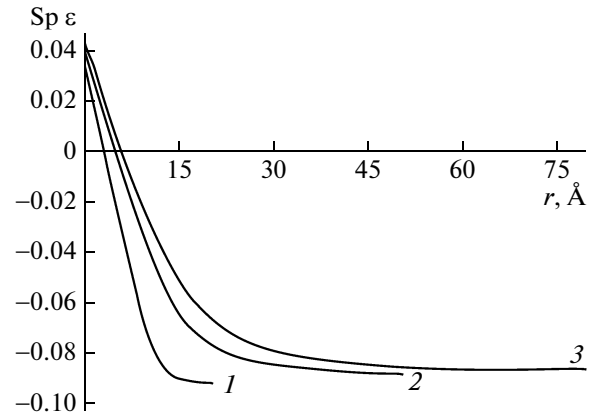


Fig. 3. Hydrostatic strain of the InAs QD material with an interstitial Bi^{3+} impurity for different QD radii: $R_0 =$ (1) 2, (2) 5 and (3) 8 nm.

The steadily decreasing dependence $\text{Sp}\varepsilon^{(1)} = f(R_0)$ results from the fact that the effect of surface forces of the Laplace pressure (formula (4)) is less profound for QDs larger in size.

From Figs. 2 and 3, it follows that, because of the impurity in the QD, the distribution of strains is spatially inhomogeneous, which brings about the appearance of a force $F(x) = \theta_d \frac{\partial \varepsilon(x)}{\partial x}$ acting upon the defect [24]. This force induces an additional strain-induced atomic flux $j_d = v N_d$, where $v = \frac{D \theta_d \partial \varepsilon(x)}{k T \partial x}$ is the

velocity of atoms that move due to the strain gradient in the QD (D is the diffusion coefficient, k is the Boltzmann constant, T is temperature, $\theta_d = K_A \Delta \Omega$ is the deformation potential, and K_A is the elasticity modulus). The direction of the atomic flux depends on the signs of the deformation potential and strain gradient; i.e., defects that are stretching centers ($\theta_d > 0$) are accumulated in the region of relative stretching strains in the material, whereas defects that are compression centers ($\theta_d < 0$) are accumulated in the region of relative compressive strains. Since the covalent radius of In is larger than that of Ga, the In atoms can be considered as stretching centers. The strain-induced flux opposite in direction to the normal gradient-related flux promotes the localization of In atoms in the QD and, correspondingly, limits their migration mobility. This effect is bound to manifest itself as an improvement in the uniformity of the size of QDs, which is observed experimentally [25].

In addition, the Bi impurity embedded in the QD changes the average strain ($\bar{\varepsilon} = \frac{4\pi}{V} \int_0^{R_0} \text{Sp}\varepsilon(r) r^2 dr$,

where V is the QD volume) and, correspondingly, the surface energy of the array of coherently strained 3D islands. In [3], it was shown that the character of

the dependence of the surface energy on the island size depends on the parameter α (formulas (14), (15) in [3]) which is equal to the relative change in the surface energy upon the formation of one island. The change in the strain due to the Bi impurity yields a decrease in the parameter α and, consequently, the system of islands becomes more stable to coalescence [3].

4. CONCLUSIONS

In this study, a theoretical model of strains in spherical QDs doped with an isovalent impurity is developed. This model allows a qualitative explanation of the experimental data on the production of an array of homogeneous InAs QDs doped with Bi [25]. Bismuth is an electrically inactive impurity; i.e., it does not increase the charge-carrier concentration. However, bismuth substantially modifies the conditions of QD formation by inducing a diffusion-strain flux. In this case, the function of bismuth is to limit the migration mobility of In and As atoms upon the self-assembly of the QD layer and to influence the surface energy. It is established that it is possible to substantially suppress the coalescence process and, in this way, to improve the degree of size uniformity of the islands, if InAs is doped with the Bi impurity isovalent to As during deposition. Thus, doping of the InAs QD layer with Bi during its formation and self-assembly on the GaAs surface facilitates the growth of islands (QDs) more uniform in size. Further development of the model will involve consideration for the role of the wetting layer and for the influence of the Bi dopant impurity on dislocated clusters that are the main defects in QD heterostructures.

REFERENCES

1. L. E. Vorob'ev, V. Yu. Panevin, N. K. Fedosov, D. A. Firsov, V. A. Shalygin, A. D. Andreev, Yu. B. Samsonenko, A. A. Tonkikh, G. E. Cirilin, N. V. Kryzhanovskaya,

- V. M. Ustinov, S. Hanna, A. Seilmeier, N. D. Zakharov, and P. Werner, *Semiconductors* **39**, 41 (2005).
2. V. V. Svetukhin, S. V. Bulyarskii, and D. V. Sanchishchin, *Tech. Phys. Lett.* **30**, 220 (2004).
3. N. N. Ledentsov, V. M. Ustinov, V. A. Shchukin, P. S. Kop'ev, Zh. I. Alferov, and D. Bimberg, *Semiconductors* **32**, 343 (1998).
4. V. P. Evtikhiev, O. V. Konstantinov, A. V. Matveentsev, and A. E. Romanov, *Semiconductors* **36**, 74 (2002).
5. N. N. Ledentsov, V. A. Schukin, T. Kettler, K. Posilovic, D. Bimberg, L. Y. Karachinsky, A. Y. Gladyshev, M. V. Maximov, L. I. Novikov, Y. M. Shernakov, A. E. Zhukov, V. M. Ustinov, and A. R. Kovsh, *J. Cryst. Growth* **301**, 914 (2007).
6. B. V. Novikov, G. G. Zegrya, R. M. Peleshchak, O. O. Dan'kiy, V. A. Gaisin, V. G. Talalaev, I. V. Shtorm, and G. E. Cirlin, *Semiconductors* **42**, 1076 (2008).
7. V. A. Shchukin and D. Bimberg, *Appl. Phys. A* **67**, 687 (1998).
8. V. G. Dubrovskii, Yu. G. Musikhin, G. E. Cirlin, V. A. Egorov, N. K. Polyakov, Yu. B. Samsonenko, A. A. Tonkikh, N. V. Kryzhanovskaya, N. V. Bert, and V. M. Ustinov, *Semiconductors* **38**, 329 (2004).
9. V. F. Osipov, F. Schenitt, S. A. Kukushkin, and P. Hess, *Appl. Surf. Sci.* **188**, 156 (2002).
10. V. G. Dubrovskii, G. E. Cirlin, and V. M. Ustinov, *Phys. Rev. B* **68**, 075409 (2003).
11. V. G. Dubrovskii and N. V. Sibirev, *Tech. Phys. Lett.* **31**, 161 (2005).
12. V. K. Bazhenov and V. I. Fistul', *Sov. Phys. Semicond.* **18**, 843 (1984).
13. S. K. Guba and I. V. Kurilo, *Function. Mater.* **8**, 234 (2001).
14. R. D. Vengrenovich, Yu. V. Gudyma, and S. V. Yarema, *Semiconductors* **35**, 1378 (2001).
15. V. G. Talalaev, B. V. Novikov, S. Yu. Verbin, A. B. Novikov, D. Sh. Tkhak, G. Gobsh, R. Gol'dkhan, N. Shtein, A. Golombek, G. E. Cirlin, V. N. Petrov, V. M. Ustinov, A. E. Zhukov, and A. Yu. Egorov, *Semiconductors* **34**, 453 (2000).
16. G. Chris, van de Walle, *Phys. Rev. B* **39**, 1871 (1989).
17. V. A. Shchukin, N. N. Ledentsov, P. S. Kop'ev, and D. Bimberg, *Phys. Rev. Lett.* **75**, 2968 (1995).
18. Z. M. Wang, K. Holmes, Yu. I. Mazyr, and G. J. Salamo, *Appl. Phys. Lett.* **84**, 1931 (2004).
19. A. Qteish and R. J. Needs, *Phys. Rev. B* **45**, 1317 (1992).
20. K. Teodosiu, *Elastic Models of Crystal Defects* (Springer, Berlin, Heidelberg, New York, 1982; Mir, Moscow, 1985).
21. N. Moll, M. Scheffler, and E. Pehlke, *Phys. Rev. B* **58**, 4566 (1998).
22. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 7: *Theory of Elasticity* (Nauka, Moscow, 1982; Pergamon Press, New York, 1986).
23. A. M. Kosevich, *Theory of Crystal Lattice* (Vishcha Shkola, Kiev, 1988) [in Russian].
24. V. I. Emel'yanov and I. M. Panin, *Phys. Solid State* **39**, 1815 (1997).
25. B. N. Zvonkov, I. A. Karpovich, N. V. Baidus', D. O. Filatov, and S. V. Morozov, *Semiconductors* **35**, 93 (2001).

Translated by E. Smorgonskaya