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LOW-DIMENSIONAL SYSTEMS

Effect of In and Al Content on Characteristics of Intrinsic Defects in GaAs-Based Quantum Dots

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Abstract—The effect of In and Al on the properties of the As_{Ga} defect complex (arsenic substituted for gallium at a crystal lattice site) in GaAs-based quantum dots (QDs) was investigated using the nonempirical quantum-chemical SCF–MO–LCAO technique. It is shown that an As_{Ga} defect can exist in stable and metastable states. Raising the indium or aluminum content in QD enhances the probability of As_{Ga} defect formation in the stable state; in case of In introduction, this effect is manifested more strongly. The activation energy of the transition between stable and metastable states varies between 0.886 and 2.049 eV, depending on the QD stoichiometry. The formation of an As_{Ga} defect gives rise to two deep levels in the band gap. © *2004 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

The formation of In(GaAs) quantum dots (QD) by self-organized growth is accompanied by the generation of structural defects, which can affect the characteristics of optoelectronic devices with quantum-confined active layers [1–6]. One of these defects is an intrinsic defect designated in the literature as *EL2* [5, 7, 8]. It is observed in both doped and undoped GaAs, and its concentration can be high.

In the literature there is no unanimous opinion about not only the atomic composition of the *EL2* defect, but also its influence on the electronic and optical properties of crystals. It is pointed out that *EL2* exhibits thermal and optical metastability associated with the structural reconstruction of the defect [9, 10]. It is assumed that the defect is an As_{Ga} complex (an As atom substitutes for Ga at a crystal lattice site) and its aggregations with other defects in GaAs [11–13]. It has been suggested [14] that the metastability of an *EL2* defect may be related to the transfer of an As atom from the lattice site normally occupied by the Ga atom to an interstice, with the formation of a complex including As_{Ga} and a Ga vacancy. The influence of the content of impurity atoms capable of entering into the composition of GaAs-based QDs on the *EL2* characteristics has not been studied.

This paper is devoted to studying the influence of In and Al content on the properties of an As_{Ga} defect in GaAs-based QDs. The process of defect formation was investigated using the nonempirical quantum-chemical SCF–MO–LCAO approach (the self-consistent field method, which represents each molecular orbital as a linear combination of atomic orbitals). The computer simulation was performed in the cluster approximation; i.e., a limited fragment was cut from the crystal lattice, with the initial positions of atoms corresponding to their positions at the sites of an actual lattice.

2. CALCULATION PROCEDURE

The parameters of the As_{Ga} defect were calculated using the GAMESS software package [15, 16]. The basis set MINI was used, which enables one to calculate the energy of chemical bonds and intermolecular interactions in crystalline compounds quite precisely [17]. A 26-atom fragment of crystal lattice of a GaAs-based QD was chosen as a cluster model (Fig. 1). The dangling bonds at the cluster boundary were satisfied with hydrogen (30 atoms); this excluded distortions of the electronic structure related to the effect of unpaired electrons on the cluster surface. The boundary hydrogen atoms make it possible to approximately take into account the interface between the QD and the matrix in the modeling.

To model an intrinsic point defect As_{Ga}, a Ga atom at the lattice site (in the center of the cluster) was replaced by an As atom. The length of the Ga–As bond in the cluster was chosen as 2.44 Å, so that the lattice constant was matched with the lattice constant of bulk GaAs crystal, 5.65 Å. The effect of In or Al content on the characteristics of such a defect was simulated by replacing a part of the Ga atoms by Al or In atoms in a specific percentage amount (from 10 to 40%).

To calculate the defect structure, a full gradient optimization of the cluster geometrical parameters (bond lengths, valence and torsion angles) within the first

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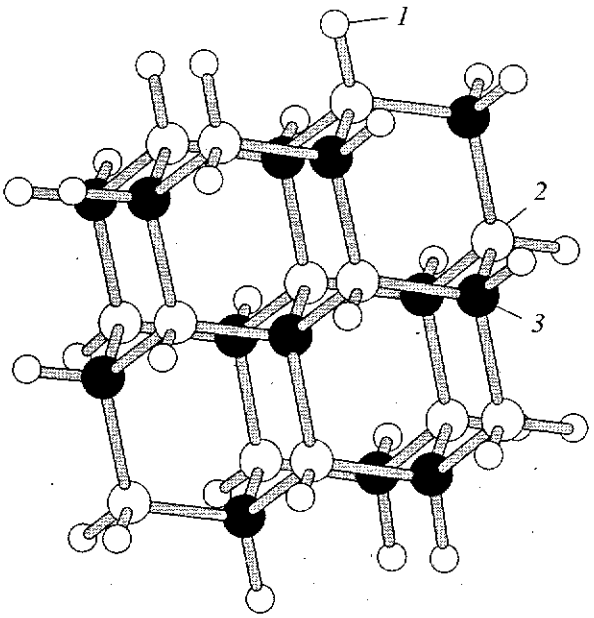

Fig. 1. A model of a 26-atom GaAs cluster. Atoms: (*1*) H, (*2*) Ga, and (*3*) As.

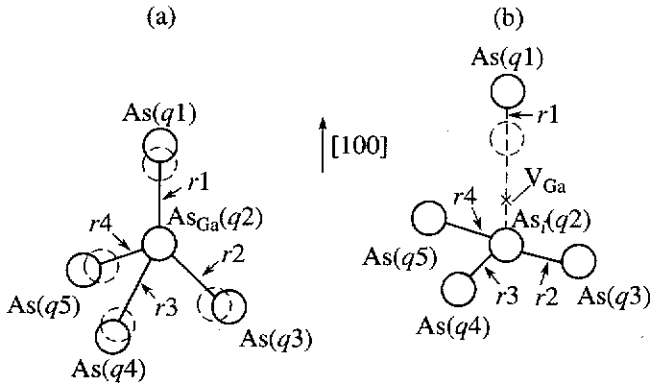

Fig. 2. The structure of an As_{Ga} defect as obtained in the calculation of GaAs, $Al_{1-x}Ga_xAs$, and $In_{1-x}Ga_xAs$ clusters: (a) stable, (b) metastable state.

coordination sphere was done. This approach allows one to determine the crystal lattice relaxation in the defect region, taking account of the crystal field of the environment.

3. RESULTS AND DISCUSSION

The calculation of the parameters of GaAs clusters containing Al and In allowed us to reveal two minima, which differ in energy, on the potential energy surface of the system. It appeared that they correspond to two relatively stable structural states of the As_{Ga} defect in the cluster, which hereinafter we will refer to as "stable" and "metastable." Similar defect structures were discussed in [18] for the case of undoped GaAs.

Figure 2 shows the structures corresponding to stable and metastable states of an As_{Ga} defect, and Table 1 lists interatomic distances r and charges q on atoms incorporated into clusters: GaAs, $Al_{0.1}Ga_{0.9}As$, $Al_{0.2}Ga_{0.8}As$, $Al_{0.4}Ga_{0.6}As$, $In_{0.1}Ga_{0.9}As$, $In_{0.2}Ga_{0.8}As$, and $In_{0.4}Ga_{0.6}As$.

As is seen in Fig. 2, the lattice structure in the vicinity of the defect is distorted when an As atom is substituted for Ga at the lattice site. When the stable state is formed, all the As_{Ga}–As bonds are slightly elongated compared to the Ga–As bond, symmetrically in all directions (Fig. 2a, Table 1). After relaxation of the nearest environment, the As_{Ga} atom remains at the lattice site owing to the lower strength of the As_{Ga}–As bond in comparison with the Ga–As bond. In the metastable state of an As_{Ga} defect, three As atoms remain in their places, and the fourth, which has a lowered coordination number, is shifted toward the plane in which the three Ga atoms bonded to it lie (Fig. 2b, Table 1). The As atom replacing Ga is shifted toward the interstice and is located just below the plane containing three As atoms bonded to it. The metastable state of an As_{Ga} defect can be considered as a complex comprising a Ga vacancy V_{Ga} and an interstitial As atom.

The analysis of the distribution of charge on atoms in a GaAs cluster that models the defect-free lattice shows that an As atom at a site is charged negatively ($-0.32\bar{e}$). This means that an As atom accepts part of the electron density from Ga atoms. In the metastable state of an As_{Ga} defect, the charge on the As atom is virtually zero ($q2 = +0.06\bar{e}$, Table 1), with As in a trivalent state typical of its covalent molecular compounds.

With the formation of a defect, the distribution of charges in a cluster is modified. In the stable state of an As_{Ga} defect, the As atom is at the lattice site; it forms four As–As bonds. As is seen in Table 1, in this case the As atom accepts a considerable positive charge $q2 = +0.35\bar{e}$; in other words, a large part of the electron density is transferred from the As_{Ga} atom to neighboring atoms. This redistribution of the electron density can give rise to deep donor levels in the energy gap of (Al,Ga)As crystal; they can be related to the *EL2* defect [5, 7, 8].

One should note that the total charge of an As_{Ga} defect is nearly the same for stable and metastable states, but its distributions between the atoms in the defect region are substantially different in different states. The addition of Al or In atoms to a GaAs lattice does not significantly change the charges on atoms and the structural parameters of the defect, neither in the stable nor in the metastable state (Table 1). At the same time, the energy parameters of an As_{Ga} defect are noticeably modified when the content of aluminum or indium in a GaAs lattice increases.

The difference between the energies of stable and metastable state ΔE and the activation energy E_a of the transition from the stable to the metastable state of an

Table 1. Interatomic distances and atomic charges in relation to Al and In content for stable and metastable states of an As_{Ga} defect in GaAs, $Al_xGa_{1-x}As$, and $In_xGa_{1-x}As$

Compound	Stable state								
	interatomic distances, Å				atomic charges, elementary charge units				
	r^1	r^2	r^3	r^4	q^1	q^2	q^3	q^4	q^5
GaAs	2.60	2.59	2.60	2.59	−0.48	+0.35	−0.38	−0.39	−0.39
$Al_{0.1}Ga_{0.9}As$	2.60	2.59	2.60	2.60	−0.49	+0.35	−0.38	−0.39	−0.39
$Al_{0.2}Ga_{0.8}As$	2.60	2.59	2.60	2.60	−0.49	+0.35	−0.38	−0.40	−0.39
$Al_{0.4}Ga_{0.6}As$	2.60	2.59	2.60	2.60	−0.49	+0.35	−0.40	−0.40	−0.39
$In_{0.1}Ga_{0.9}As$	2.60	2.56	2.61	2.56	−0.40	+0.35	−0.38	−0.40	−0.50
$In_{0.2}Ga_{0.8}As$	2.63	2.54	2.55	2.55	−0.42	+0.35	−0.41	0.37	−0.51
$In_{0.4}Ga_{0.6}As$	2.63	2.54	2.53	2.58	−0.42	+0.36	−0.40	−0.40	−0.52
	Metastable state								
GaAs	3.46	2.43	2.43	2.43	−0.50	+0.06	−0.24	−0.36	−0.24
$Al_{0.1}Ga_{0.9}As$	3.46	2.43	2.43	2.43	−0.50	+0.06	−0.24	−0.38	−0.24
$Al_{0.2}Ga_{0.8}As$	3.46	2.43	2.43	2.43	−0.50	+0.06	−0.24	−0.26	−0.24
$Al_{0.4}Ga_{0.6}As$	3.46	2.43	2.43	2.43	−0.50	+0.06	−0.26	−0.26	−0.38
$In_{0.1}Ga_{0.9}As$	3.48	2.41	2.40	2.40	−0.50	+0.06	−0.23	−0.40	−0.24
$In_{0.2}Ga_{0.8}As$	3.50	2.40	2.39	2.39	−0.51	+0.06	−0.23	−0.40	−0.27
$In_{0.4}Ga_{0.6}As$	3.49	2.40	2.39	2.38	−0.51	+0.07	−0.29	−0.27	−0.40

Table 2. The difference between the energies of stable and metastable state ΔE and the activation energy E_a of the transition from the stable to the metastable state of an As_{Ga} defect with different Al or In content in GaAs, $Al_xGa_{1-x}As$, and $In_xGa_{1-x}As$

	GaAs	$Al_{0.1}Ga_{0.9}As$	$Al_{0.2}Ga_{0.8}As$	$Al_{0.4}Ga_{0.6}As$	$In_{0.1}Ga_{0.9}As$	$In_{0.2}Ga_{0.8}As$	$In_{0.4}Ga_{0.6}As$
ΔE, eV	0.70	0.71	0.73	0.74	0.85	0.88	0.90
E_a, eV	1.05	1.86	1.86	0.97	2.05	0.89	1.84

As_{Ga} defect are listed in Table 2 for different Al or In content in GaAs, $Al_xGa_{1-x}As$, and $In_xGa_{1-x}As$. The quantity ΔE characterizes the relative probability of the formation of structures corresponding to stable and metastable defect states in the crystal. As follows from Table 2, the rise of Al or In content raises the probability that an As_{Ga} defect will occur in a stable state. This effect is manifested more strongly when In atoms are introduced into the crystal.

To estimate E_a, the structures of the corresponding transition states were calculated. These structures were defined based on the conjectured path of As atom transfer from a site to an interstice (stable to metastable state of the defect), taking the lattice symmetry into account. Figure 3 shows schematically the displacement of an As atom from the lattice site to an interstice, which corresponds to the transition of a defect from the stable to the metastable state. For each of the clusters that model different In or Al content in the lattice, the calculations revealed on the potential energy surfaces extremal points corresponding to the structures in which the As atom lies in the plane of the three As atoms bonded to it. The activation energy E_a was determined as the difference between the total energies of the cluster at the extremal point (transition state) and in the stable state.

It is seen from Table 2 that the introduction of In or Al into a GaAs crystal lattice raises the activation energy of the transition between the stable and the metastable state of the defect. The nonmonotonic dependence of E_a on In content may indicate the influence of In distribution in the crystal to the activation energy. To obtain better estimation of the E_a dependence on In content, is seems necessary to raise the number of atoms in clusters. For an Al content of 10–20%, the activation energy remains virtually unchanged. At the same time, the activation energy sharply decreases at 40% Al, which may indicate a considerable modification of energy characteristics of the crystal lattice in the defect region.

The limited size of the clusters used in the study give no way of describing precisely the band structure of the materials under study. Nevertheless, the contribution of an As_{Ga} defect to the electronic structure of the cluster was estimated based on the calculated eigenenergies and eigenvectors of the corresponding molecular orbitals. It appeared that this defect gives rise to two deep

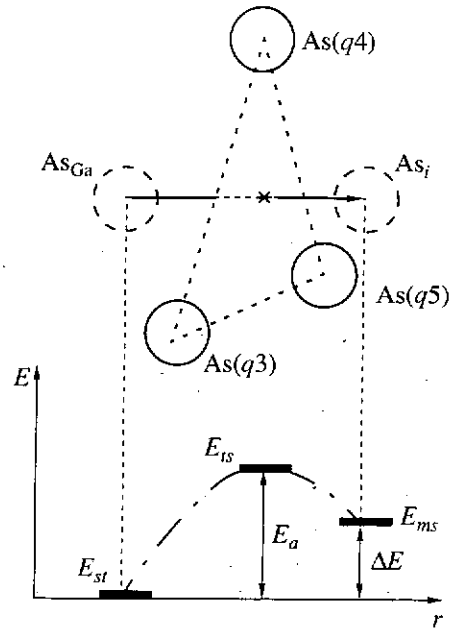

Fig. 3. Schematics of the defect transition from stable (As_{Ga}) to metastable ($As_i + V_{Ga}$) state: E_{st} is the total energy of the cluster in the stable state; E_{ts}, the energy of the transition state; E_{ms}, the total energy of a metastable state. The sign × marks the position of the As atom corresponding to the transition state.

levels in the band gap, which qualitatively agrees with the results of [14]. According to our estimates, the positions of these levels in respect to the top of the valence band in undoped GaAs are $E_{S1} = 0.40$ eV, $E_{S2} = 1.26$ eV for the stable and $E_{M1} = 0.23$ eV, $E_{M2} = 1.32$ eV for the metastable state. The addition of In or Al only slightly affects the positions of E_{S1}, E_{S2}, and E_{M1} levels, whereas the energy E_{M2} decreases by 0.26 eV. At a 40% In/Al content, only one level E_{M1} appears in the metastable state of a As_{Ga} defect.

4. CONCLUSION

The effect of In and Al content on the properties of As_{Ga} defects in GaAs-based QDs has been investigated using the nonempirical quantum-chemical SCF–MO–LCAO technique. It is shown that a As_{Ga} defect can exist in stable or metastable states, which differ in their structural, electronic, and energy characteristics. Increasing the In or Al content enhances the probability that the As_{Ga} defect will form in the stable state; this effect is manifested more strongly in the case of In introduction into a QD. The activation energy of the transition between the stable and the metastable state varies between 0.886 and 2.049 eV, depending on the QD stoichiometry. The formation of an As_{Ga} defect gives rise to two deep levels in the band gap, whose positions are also dependent on the introduction of In or Al.

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