Interface defects and silicon impurities in GaAs/Al\textsubscript{0.3}Ga\textsubscript{0.7}As heterostructures

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Abstract. The formation of complex defects (gallium, arsenic and aluminium vacancies with corresponding interstitial atoms) present at the GaAs/Al\textsubscript{0.3}Ga\textsubscript{0.7}As heterointerface as well as passivation of the defects by silicon impurities are discussed in the report. We used the density functional theory calculations, with the hybrid functionals B3LYP with Hay-Wadt effective core potentials for all the heavy atoms, in combination with Hay-Wadt valence basis. We present the energy characteristics (formation energy) and geometry of the defects (spatial distribution of the atoms and its charge near the interface defect).

1. Introduction

Infrared photodetectors based on GaAs/AlGaAs quantum wells (absorption wavelength range of 8-10 μm) are widely used for development of military thermal vision systems. One of the main requirements for the systems is reliability which depends on the presence and characteristics of defects in the GaAs/AlGaAs heterostructure. Point defects, as well as the doping process, are of great interest due to the influence on the structure of quantum wells of GaAs/AlGaAs, as well as changes in the processes of charge transfer and energy levels. With the change in the structure of quantum wells, the parameters of infrared photodetectors change [1].

The main alloying impurities in GaAs/AlGaAs are silicon and carbon. Doping of AlGaAs barriers by Si atoms not only leads to a change in the structural, but also optical properties in the infrared spectral range. In the absorption spectra of GaAs/AlGaAs heterostructure additional bands arise, associated with the appearance of complex defects involving silicon. On the other hand doping of AlGaAs by Si can lead to passivation of structural defects (vacancies) which leads to improving reliability of the devices based on GaAs/AlGaAs heterostructure.

This paper presents the energy characteristics, as well as the spatial distribution of the defect complexes in the GaAs/AlGaAs heterostructure of quantum well infrared photodetectors (QWIP).

2. Methods of Calculation

To determine the energy and structural characteristics of point defects, the cluster approximation method was used [2]. For the GaAs/AlGaAs cluster, the GaAs crystal lattice (zinc blende) was chosen, with lattice constant at 300 K [3]. The model clusters were formed by “cutting” the bounded fragment...
from the GaAs crystal volume [4]. AlGaAs was modelled by replacing the gallium atoms by aluminium atoms (in a percentage ratio of about 30%), taking into account the growth of the real crystal (in our case, the growth plane of GaAs is (100)) [5]. The cluster GaAs/AlGaAs consisted of 72 arsenic atoms, 62 gallium atoms and 10 aluminium atoms (total 144 atoms). The bonds on the cluster boundary were closed by hydrogen atoms, with the aim of eliminating distortion of the structure and improving the values of convergence [4].

Geometry optimization of the cluster was carried out on the base of the density functional theory (with the hybrid functional B3LYP1 and the relativistic Hay-Wadt potentials). Atomic orbitals were given by the basic kit Hay-Wadt [6]. Calculations were made in the software package FireFly [7]. Complexes of defects were created at the interface of the well/barrier GaAs/Al$_{0.3}$Ga$_{0.7}$As by transferring the atom from the crystal lattice site (interstitial atoms), as well as removing the atom from the lattice site and adding an interstitial silicon atom (for the vacancy – interstitial silicon atom complexes). The full geometry optimization with respect to total energy minimization was performed after construction of the model cluster (gradient convergence tolerance for the calculation was taken as 0.00001 Hartree/Bohr (this value is optimal for the clusters based on $A_3B_5$ compounds [8, 9]). The formation energies of the defect complexes were determined by the difference in the total energy of the defect-free cluster relative to the total energy of the optimized defective cluster.

3. Results and discussion

In the case of the gallium atom moved to the interstitial position within the first coordination sphere, the cluster geometry optimization leads to annihilation of the vacancy with an interstitial gallium atom [10]. This means that the defect is not stable. Thus, to determine the stable configuration of defects it is appropriate to consider the complex of defects, namely, vacancy + the interstitial atom in second coordination sphere, for example, the complex of the gallium vacancy $V_{Ga}$ and its interstitial atom Ga$_i$ in the crystallographic plane (100), as shown on figure 1.

For above motioned complex defect the arsenic atom (2) moves to the $V_{Ga}$ position, the gallium atom (1) replaces the arsenic atom (2) during the geometry optimization procedure. As a result, two anti-structural defects of As$_{Ga}$ and Ga$_{As}$ are formed [11]. The gallium atom (3) moves to the interstitial position, Ga$_i$ as a defect is preserved. The energy of formation of this complex is 4.9295 eV [12].

The interatomic distances for the initial cluster ($r_i$) and the geometrically optimized model ($r_o$) for a cluster with Ga$_i$ – $V_{Ga}$ defect complex are shown in table 1. The distances $r_o$ represent the spatial parameters of the defect and can be determined on the base of experimental investigations, for example, using extended X-ray absorption fine structure spectroscopy [9].
Table 1. Interatomic distances of cluster Ga_i – V_{Ga} defect complex.

| r_c, Å | 2-1 | 1-4 | 4-3 | 4-2 |
|--------|-----|-----|-----|-----|
| 1.28   | 1.80| 4.00| 2.45|
| 2.64   | 2.57| 2.60| 4.15|

A complex of defects “arsenic vacancy V_{As} and its interstitial atom As_i” in the crystallographic plane (100) is shown on figure 2.

In the process of geometric optimization, two vacancy-interstitial arsenic (As_i-V_{As}) complexes are formed. Atom 1 moves to the interstitial position, but its place remains the vacancy of arsenic. The energy of formation of this complex is 6.034 eV [13]. The interatomic distances for the initial cluster (r_c) and the geometrically optimized model (r_o) for a cluster with As_i – V_{As} defect complex are shown in table 2.

Table 2. Interatomic distances of cluster As_i – V_{As} defect complex.

| r_c, Å | 2-1 | 2-4 | 1-3 | 3-4 |
|--------|-----|-----|-----|-----|
| 1.44   | 1.73| 2.45| 4.00|
| 2.49   | 2.54| 2.57| 4.70|

To investigate the possibility of passivation of V_{As} and V_{Ga} by silicon impurity the complex of defects “vacancy and the interstitial silicon atom Si_i” were considered. The defects “gallium vacancy and the interstitial silicon atom Si_i” is shown in figure 3.

Table 2. Interatomic distances of cluster As_i – V_{As} defect complex.
In the process of geometric optimization, a more complex defective complex appears: Si, and the complex $V_{Ga}$ and $Ga_i$. The atom (2) moves to the interstitial position, $V_{Ga}$ remains in its place. The charge density of cluster with $Si_i - V_{Ga}$ defect complex in the crystallographic plane (011) is shown of figure 4. The charge distribution in the vicinity of the defect can be used to calculate the defect charge and the energy levels of the defect in the GaAs/Al$_{0.3}$Ga$_{0.7}$As quantum well (the energy levels determine absorption spectrum of the QWIP).

![Figure 4](image)

**Figure 4.** The charge density of cluster with $Si_i - V_{Ga}$ defect complex.

At is seen in figure 3 and 4 the charge of the silicon atom does not correspond to the lattice position of atoms (for example, arsenic and gallium), which confirms the preservation of the interstitial silicon atom as a defect. The interatomic distances for clusters with $Si_i - V_{Ga}$ defect complex are shown in table 3.

|       | 2-1 | 1-4 | 2-3 | 3-4 |
|-------|-----|-----|-----|-----|
| $r_c$, Å | 1.79 | 3.54 | 2.45 | 5.65 |
| $r_o$, Å | 2.51 | 2.48 | 2.52 | 5.97 |

The defect complex “arsenic vacancy and the interstitial silicon atom” in the crystallographic plane (100) is shown on figure 5.

![Figure 5](image)

**Figure 5.** Model cluster with $Si_i - V_{As}$ defect complex.
For this case in the process of geometric optimization the interstitial silicon atom annihilates with an arsenic vacancy (atom 1 replaces $V_{As}$), resulting in the formation of an anti-structural defect of $Si_{As}$ [14]. This means that silicon impurity passivates the arsenic vacancy. The charge density of cluster with $Si_i - V_{As}$ defect complex in the crystallographic plane (100) is shown of figure 6.

![Figure 6. The charge density of cluster with $Si_i - V_{As}$ defect complex.](image)

On the base of the distribution of the charge in the near-defect region cluster with the defect $Si_i - V_{As}$ one can conclude that the charge of the silicon atom roughly corresponds to the charge of the lattice atom of arsenic (this fact confirms the occurrence of a new $Si_{As}$ defect in the process of geometric optimization). The interatomic distances for clusters with $Si_i - V_{As}$ complex defects are shown in table 4.

|       | 2-1 | 1-3 | 1-4 | 2-4 |
|-------|-----|-----|-----|-----|
| $r_c$, Å | 2.31 | 1.46 | 3.58 | 2.45 |
| $r_o$, Å | 5.02 | 4.20 | 5.99 | 2.58 |

4. Conclusions
On the base of the calculations carried out, it was shown that stable complex defects $As_i - V_{As}$ and $As_{Ga} + Ga_{As}$ are formed in $GaAs/Al_{0.3}Ga_{0.7}As$ heterostructure. It was ascertained that an impurity silicon atom passivates the vacancy of an arsenic atom, but does not passivates the vacancy of a gallium atom. Thus, the alloying of the barrier layer of $GaAs/Al_{0.3}Ga_{0.7}As$ quantum well by silicon atoms leads to improving reliability of $GaAs/AlGaAs$ quantum well infrared photodetector when the QWIP is used under a radiation influence conditions (for the radiation flux which causes an arsenic vacancy formation). The charge states of silicon impurities in the $GaAs/Al_{0.3}Ga_{0.7}As$ heterostructure were calculated also. The data obtained can be used for simulation of the QWIP absorption spectrum.

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