ISSN 2635-1676, Nanobiotechnology Reports, 2024, Vol. 19, No. 2, pp. 225–229. © Pleiades Publishing, Ltd., 2024.
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NANOMATERIALS FOR FUNCTIONAL AND STRUCTURAL PURPOSES

Theoretical Modeling of Indium Adatoms on Reconstructed GaAs(001) and AlAs(001) Surfaces

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Received December 5, 2023; revised December 22, 2023; accepted December 22, 2023

Abstract—GaAs/AlAs(001) (2 × 4) is one of the most optimal substrates for optoelectronic and nanophotonic applications. Droplet epitaxy allows high-quality quantum dot (QD) arrays with the desired properties to be obtained, but the detailed mechanism of deposition and subsequent epitaxial growth is still questionable. In this paper, the growth mechanism of indium QDs on various GaAs/AlAs(001) surfaces is studied within calculations of density functional theory. Full geometry optimization, in which the coordinates of substrate atoms can be altered under adatom impact, is shown to be a straightforward technique for the simulation of adsorption processes. The obtained results are in good agreement with conventional methods and well-known findings. The proposed approach could become standard practice and extend the understanding of droplet epitaxy.

DOI: 10.1134/S2635167623601328

INTRODUCTION

Arrays of semiconductor quantum dots (QD) are of great importance due to their promising optoelectronic and nanophotonic applications. Droplet epitaxy is a two-stage growth mechanism of molecular-beam epitaxy, which supposes the formation of metallic droplets at the first stage and their subsequent crystallization during second nonmetallic component deposition. Such an approach widens the set of materials suitable for the formation of QDs and allows strain-free structures with independent control of their size, surface density, and chemical composition to be achieved [1]. However, the mechanism of droplet nucleation, the formation of ensembles, and the subsequent growth of islands are still quite poorly investigated [2, 3]. Moreover, growth in droplet epitaxy can take place by both the Stranski–Krastanov and Volmer–Weber mechanisms depending on the experimental conditions and therefore the exact type of growth mode implemented remains unclear [4].

GaAs(001) is one of the most suitable semiconductor surfaces for practical application in the majority of optoelectronic and nanophotonic devices [5, 6]. Depending on the deposition method and synthesis conditions, especially stoichiometry, the GaAs(001) surface demonstrates a great variety of surface reconstructions [7–10]. The arsenic-terminated GaAs(001) (2 × 4) reconstruction with As dimers formed on the surface is of particular interest not only because of its importance for the epitaxial growth of GaAs, but also since deposition is usually carried out in an overpressure of arsenic resulting in an As rich phase [11, 12].

In many works the processes of deposition in droplet epitaxy have been considered in terms of methods of many-particle simulation [4, 13, 14] or single-adatom adsorption energy [11, 15–17]. The latter usually utilize preconstructed fixed surface models and just evaluate the adsorption energy of an adatom in some specific positions to find the most energetically favorable one. Such an approach does not entirely simulate the adsorption process since the coordinates of substrate atoms remain fixed and cannot be altered under the impact of adatom adsorption.

In this work, the growth mechanism of indium QDs on various GaAs/AlAs(001) surfaces is studied. Theoretical modeling is carried out to describe the behavior of an adatom, which acts as the initial nucleus for the formation of a QD and to evaluate its mobility during the deposition process. During geometry optimization the adatom is adsorbed by the surface and occupies the most energetically favorable position, which causes structural rearrangement of a few substrate surface layers. The adsorption energy of the In adatom on substrates with different configurations of additional Ga- and Al-atom single layers and a wetting layer (the same type of atoms as the adsorbate) is estimated within calculations of density functional theory (DFT).

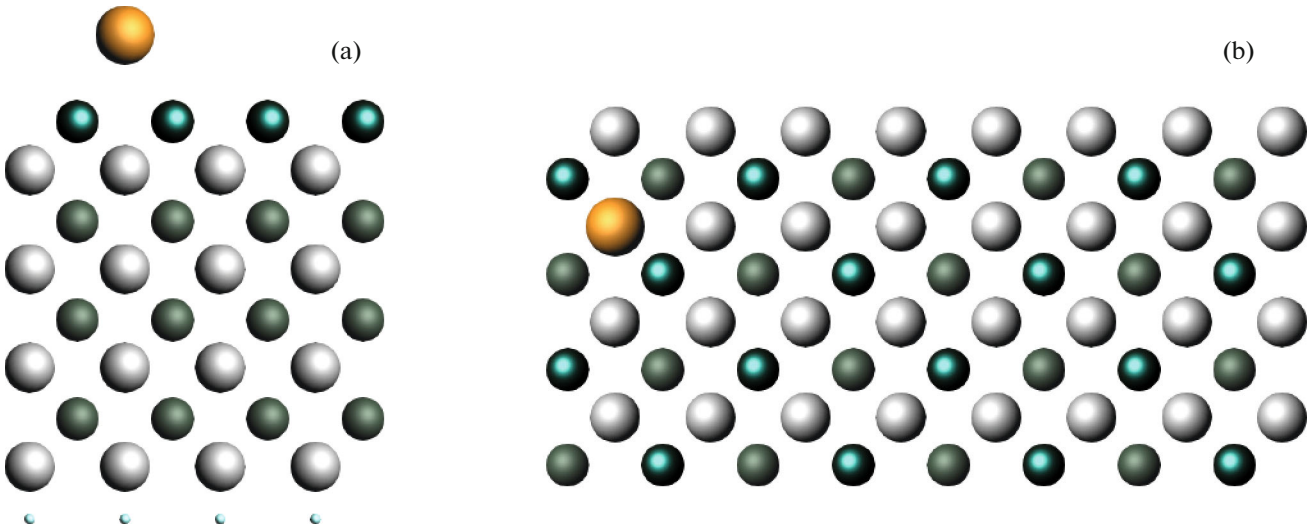

Fig. 1. Resulting structure of the 2 × 4 GaAs(001) reconstruction: (a) side view and (b) top view, where In atoms are colored yellow, the top layer of As is cyan, the other As layers are green, Ga is white, and H is blue.

THEORETICAL MODELING

Calculation Method

Quantum-chemical calculations were performed using Amsterdam Modelling Suite (BAND 2021.105) software [18]. Geometry optimization and adsorption-energy evaluation were performed using DFT. The triple-ζ basis set with the polarization function was used within the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional. To speed up calculations, a part of the core orbitals was fixed and not taken into account in the calculations. The electronic-structure self-consistency procedure involved orbitals 4*d*, 5*s*, and 5*p* for indium atoms, 3*d*, 4*s*, and 4*p* for gallium and arsenic atoms, and 2*s*, 2*p*, 3*s*, and 3*p* for aluminum atoms. In this approach, the core orbitals of each atomic element were calculated only once for a single atom and kept fixed during further calculations. The *K*-point grid in three-dimensional reciprocal space used for Brillouin-zone integration had a size of 1 × 1 × 1. The spin polarization of a free indium atom was not taken into consideration.

Structural Models

The calculation parameters had been optimized based on the periodic structures of GaAs (COD no. 9008845) and AlAs (COD no. 9008830) cubic crystals [19]. The main criteria were best agreement of the lattice parameter with the experimental data obtained from X-ray diffraction and the fastest calculation time.

Then, the optimized lattice parameters of both the GaAs (5.6682 Å) and AlAs (5.6658 Å) structures were used to generate a 2 × 2 × 4 supercell. Each formation of eight layers with a thickness of ~9.9 Å of the resulting periodic structure was separated from the next one along the *Z* axis by a gap of at least 23 Å. In this way, a model of the (001) (2 × 4) surface reconstruction with an arsenic-terminated layer was prepared (Fig. 1). Additionally, the resulting substrate was passivated by adding a single layer of hydrogen atoms at the bottom edge to minimize the impact of the neighboring surface. During geometry optimization, the two bottom layers of the substrate as well as hydrogen atoms were kept fixed.

The initial indium-adatom position was selected with a deliberately excessive distance to the surface to simulate the adsorption process. The adatom occupied the position between two adjacent atoms of the surface layer, the so called “bridge” position.

Adsorption Energy

The bonding energy of an adatom with the substrate (adsorption energy) was evaluated by the standard procedure according to the following equation [15, 20]:

$$E_{ads} = E_{system} - E_{adsorbent} - E_{adsorbate},$$

where $E_{adsorbent}$ is the formation energy of the initial “pure” substrate, $E_{adsorbate}$ is the energy of a single indium atom (adatom) in free space, and E_{system} is the formation energy of the optimized system with an adatom on the surface.

It is worth noting that the values obtained by this methodology are not typical for the conventional meaning of the adsorption energy, since they comprise not only the bonding of an adsorbed atom, but also the contribution from substrate relaxation. Such an approach has some advantages since it partially simulates the physical process of adatom adsorption, rather

than simply calculating the adsorption energy with a constrained (fixed) substrate.

RESULTS AND DISCUSSION

In this work several possible configurations of both GaAs (Table 1) and AlAs (Table 2) surfaces such as an arsenic- and metal-terminated pure substrate, a substrate with another metal single layer added and, finally, an As-terminated surface with a wetting layer (additional intermediate layer of indium atoms) have been considered. The energy of a single indium atom in free space (adatom) was evaluated to be 0.0112 eV and this value was then used for all calculations of the adsorption energy.

It has been revealed that a wetting layer of single-layer thickness increases the adatom-adsorption energy by 44% for a GaAs substrate (from −12.6 to −7.1) and by 45% for an AlAs substrate (from −13.2 to −7.3), showing the absolute result among all considered configurations (Tables 1 and 2, Fig. 2). In practice it leads to a higher mobility of adatoms and, subsequently, a decrease in the droplet density [4, 21]. This could be a sign that the indium adatom stays on top of the wetting layer without integrating into it and can diffuse further on the surface. Therefore, the resulting QDs should have a lower density due to the more probable formation of islands.

In contrast, the addition of an aluminum single layer on the GaAs substrate decreases the adsorption energy by 7% (from −12.6 to −13.5) in comparison with the pure surface. Moreover, analysis of the behavior of adatoms on the pure GaAs and AlAs substrates also indicates that an increased Al content leads to a 5% (−12.6 versus −13.2) lower adsorption energy.

Table 1. Results of the GaAs(001)-substrate energy calculations

Substrate	Single layer	Adatom	Energy, eV	E_{ads}, eV
GaAs			−536.2802	−12.5840
GaAs		In	−548.8530	
GaAs	Ga		−587.6848	−9.6303
GaAs	Ga	In	−597.3039	
GaAs	Al		−593.7246	−13.4974
GaAs	Al	In	−607.2108	
GaAs	In		−584.6612	−7.1057
GaAs	In	In	−591.7557	

Table 2. Results of the AlAs(001)-substrate energy calculations

Substrate	Single layer	Adatom	Energy, eV	E_{ads}, eV
AlAs			−600.2856	−13.2194
AlAs		In	−613.4938	″
AlAs	Al		−660.0736	−12.8437
AlAs	Al	In	−672.9061	″
AlAs	Ga		−653.6188	−10.1150
AlAs	Ga	In	−663.7226	″
AlAs	In		−650.4854	−7.3193
AlAs	In	In	−657.7935	″

In droplet epitaxy this leads to a decrease in the density of QDs, which is caused by an increased adatom diffusion length [22]. Such anomalous behavior and disagreement with the conventional Stranski–Krysta-

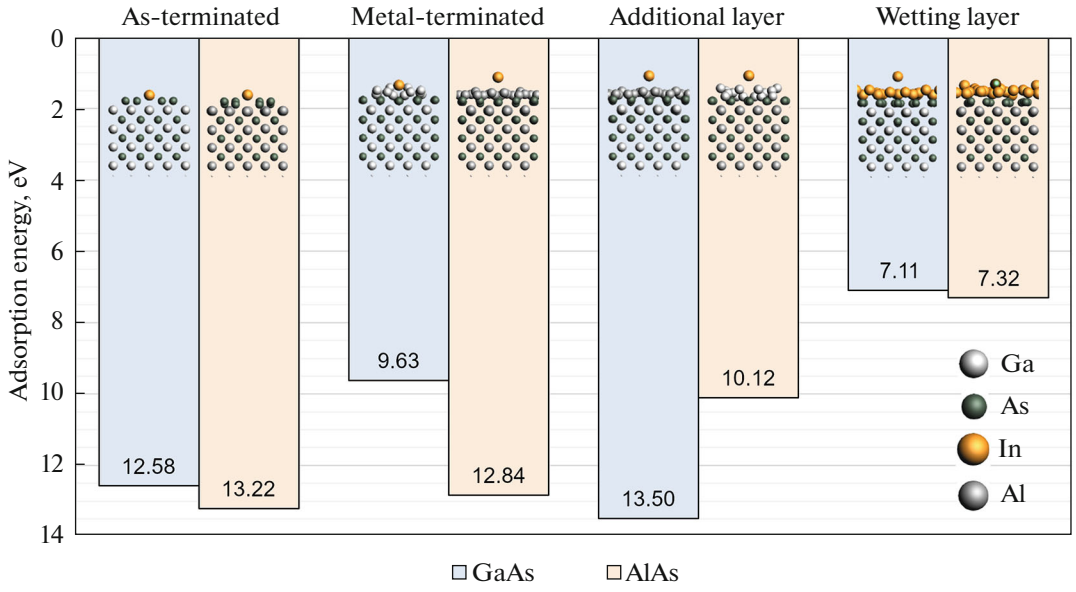

Fig. 2. Adsorption energy of an indium adatom on the different configurations of GaAs(001) and AlAs(001) surfaces.

nov growth mechanism where aluminum causes a decrease in the diffusion length due to higher chemical activity have been explained in detail using a hybrid analytical Monte Carlo model. It was noted that Al saturates the dangling bonds of the first single layer of In adatoms enabling upper indium atoms to migrate farther. The obtained results are in good agreement with this explanation. Despite the fact that the indium adatom remains at a comparatively greater distance to the surface and does not show a tendency to integration into the top layer (Fig. 2), it demonstrates a lower adsorption energy in comparison with the pure As-terminated GaAs substrate.

According to the calculations, the pure Ga-terminated GaAs surface and the AlAs substrate with an additional Ga single layer show about 24% higher adsorption energies than their precursors (from −12.6 to −9.6 and from −13.2 to −10.1, respectively). This difference probably originates from the electronegativity of the Ga–In pair, since both of the elements are metals and the formation of stable and strong bonding in such case are hardly possible. In contrast, the As–In pair in which only one element is a true metal demonstrates a much higher affinity, forming strong chemical-compound bonds.

CONCLUSIONS

Droplet epitaxy is an advanced method of obtaining high-quality quantum-dot arrays on GaAs/AlAs(001) (2 × 4) reconstructed surfaces with the desired characteristics for optoelectronic and nanophotonic applications. It has been demonstrated that complete relaxation of the substrate-atom coordinates and adatom within the DFT calculations are not only in good agreement with conventional results and other methods but could also extend the understanding of droplet epitaxy. Several configurations of both GaAs and AlAs substrates with different termination, additional single layers, and a wetting layer have been considered in terms of the adsorption energy of an indium adatom. It has been shown that a wetting layer of single-layer thickness increases the In-adatom adsorption energy by 44% for the GaAs substrate (from −12.6 to −7.1) and by 45% for AlAs (from −13.2 to −7.3), which foretells of an experimental decrease in the QD density due to the higher mobility of adatoms. In contrast, aluminum in the GaAs surface layer decreases the adsorption energy by about 7% (from −12.6 to −13.5) and in droplet epitaxy such behavior should anomalously lead to a decrease in the quantum-dot density. The gallium-terminated surfaces demonstrated a 24% higher adsorption energy due to physical-chemical nature: electronegativity of the Ga–In pair (from −12.6 to −9.6 for GaAs and from −13.2 to −10.1 for AlAs). Thus, we believe that the proposed algorithm of theoretical calculations will attract the attention of the scientific community and will be utilized for a deeper understanding of droplet epitaxy.

FUNDING

The research was financially supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment in the field of scientific activity, no. FENW-2023-0019).

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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