Energetics of growth on the $c(4\times4)$ reconstructed GaAs(001) surface and antisite formation: An *ab initio* approach

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The growth process on the As-rich $c(4\times4)$-reconstructed GaAs(001) surface via an As-Ga exchange is studied theoretically at the atomic level. Interaction energies are determined by the *ab initio* cluster method based on the Hartree-Fock formalism followed by a second-order Møller-Plesset correlation energy correction. The calculations show that the exchange process happens in three steps: (i) the As dimers in the As adsorption layer are converted to Ga-As heterodimers, (ii) the Ga atoms fill the missing dimer sites, and (iii) the Ga atoms replace the remaining As atoms in the Ga-As heterodimers. We find a stable surface structure with Ga-As heterodimers, in agreement with recent experiments. The elaborated growth sequence itself yields in addition a model for the formation of As antisite defects in the growing crystal.

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I. INTRODUCTION

Epitaxial growth of GaAs layers is of considerable interest for electronic devices.[1] In particular, growth at comparably low temperatures (200–400 °C) by molecular beam epitaxy (MBE) has the potential for designing devices with special properties.[1] The reason is that such low-temperature grown GaAs (LT GaAs) epitaxial layers are single crystalline, but nonstoichiometric due to an appreciable content of excess As. Due to the rather low growth temperatures, we can assume that this excess As is formed due to the specifics of the growth, i.e., the incorporation processes at the growing surface can play a significant role. This aspect suggests that the surface reconstruction must be taken into account. These reconstructions on the GaAs(001) surface vary considerably during MBE growth with temperature and As/Ga flux ratio. The assigned reconstructions are $c(4\times4)$, (2×4), $c(2\times8)$, (1×6), (4×6), and $c(8\times2)$ (Refs. 2–4) in order of decreasing [As]/[Ga] relative surface concentration [i.e., As/Ga relative beam equivalent pressure (BEP)]. A recent work[5] showed that under high As/Ga flux conditions, the surface structure changes to $c(4\times4)$ below 480 °C and remains unchanged down to room temperature.[5] This is just the growth parameter regime of LT GaAs. We conduct an *ab initio* calculation on the atomic level of the energetics of the *stoichiometric* growth on this $c(4\times4)$ GaAs(001) surface. Interestingly enough, our approach results in an intrinsic model for the formation of the As antisite defect that is abundant in low-temperature grown GaAs epitaxial layers.

II. MODELING APPROACH

The $c(4\times4)$ reconstructed (001) surface (Fig. 1) is modeled by unit cells which consist of three As dimers (triplet of As dimers) and one missing-dimer. This adsorption layer is bound on top of a complete As layer, equivalent to 1.75 monolayers (ML) of As surface coverage. Starting from this situation, the crystal can grow only by the incorporation of Ga atoms. On the atomic level, the incorporation of Ga atoms into the $c(4\times4)$ surface can occur in two principally different ways. One possibility is that arriving Ga atoms exchange with one or both As atoms in a surface dimer (exchange reaction, sites A–F in Fig. 1). The second possibility is that Ga atoms occupy one or both of the missing-dimer sites (attachment reaction, sites G or H in Fig. 1). In this paper, we model the growth process as a sequence of partial processes, separated by energy barriers. Starting from the As covered $c(4\times4)$ reconstructed surface, we examine by which intermediate processes and in which order Ga atoms will replace the As atoms of the adsorption layer and which stable structures can be formed during that cycle. Only single

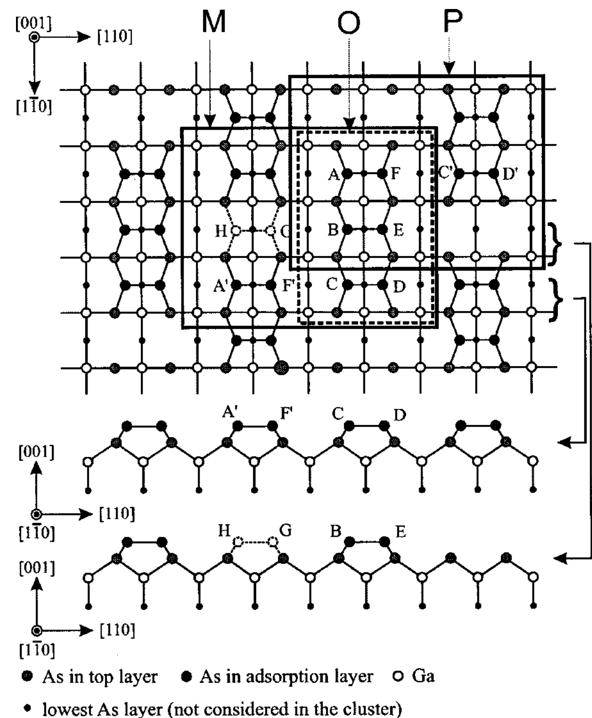

FIG. 1. The GaAs(001) reconstructed $c(4\times4)$ surface. Theoretically examined sites are labeled with capital letters. Rectangles mark the different regions modeled by clusters. The clusters comprise the upper three atomic layers (bigger circles).

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Ga atoms are offered one at a time to the surface and no additional As atoms are supplied. We determine at an *ab initio* level the energies of the involved structures and the energy barriers between them and discuss how these barriers affect the partial growth processes.

III. COMPUTATIONAL METHOD

Figure 1 shows the $c(4\times4)$ reconstructed GaAs(001) surface. Indicated by rectangular frames are three clusters that represent this surface during our calculations of the interactions of a Ga atom with different surface sites. They consist of three atomic layers, in accordance with Schailey and Ray.[6,7] In these clusters, H atoms saturate those dangling bonds that have been created when reducing the bulk GaAs crystal to the considered cluster size. No hydrogen is present on the growing (001) surface, in correspondence with the experimental conditions during molecular-beam epitaxy. The interatomic distances between the Ga and As atoms are initially chosen as the GaAs bulk equilibrium lattice constant of 5.654 Å,[8] determined experimentally. The Ga-H and As-H bond lengths are fixed to the experimentally determined values of free GaH and AsH_3 molecules[9] of 1.663 Å and 1.511 Å, respectively.

The total energies of the considered systems are determined by *ab initio* calculations. We use the Hartree-Fock (HF) method followed by a semidirect second-order Møller-Plesset (MP2) correlation energy correction to account for the many-electron systems of Ga and As atoms. The Gaussian basis set for Ga and As atoms is double zeta $\langle 14s11p5d/8s6p2d \rangle$ contracted orbitals, and that for H atoms is double zeta $\langle 4s/2s \rangle$ contracted orbitals. We calculate the total energy of the system "cluster plus approaching Ga atom" at zero temperature. The interaction energy between the cluster and the Ga atom is defined as the total energy of the system minus the sum of the total energies of the separated reactants (i.e., the Ga atom infinitely far away from the respective cluster). The applied method is similar to our earlier calculations,[10–12] in which, however, the surfaces had been left unreconstructed. Our calculations are performed with the GAUSSIAN 94 program package[13] on a Fujitsu VP parallel vector computer.

We describe the reaction pathway by stable geometric conformations with minimal energy and by the energy barriers in between them. The search for such conformations (i.e., local minima of the total energy) started from structures as given by previous results for the silicon surface[14] and additional structural elements as suggested by experience. The total energy of each of these initial structures was then minimized with the Berny geometry optimization procedure to render stable conformations with lowest total energy. The transition states between two neighboring stable conformations were determined using the synchronous transit-guided quasi-Newtonian method implemented in the GAUSSIAN 94 code. Each transition state search was always performed in forward and reverse directions. In the case in which this procedure yields the same transition states, one can conclude that no further minima exist between the actually examined neighboring states.

It is a characteristic of this type of modeling approach that in view of the available computer capacity, these extensive calculations can be performed for zero temperature only. Thus, the barrier energies that we calculate are maximum values and interpretation will be done in the framework of thermal activation. There might locally be a deviation from thermal equilibrium, for example because of slow heat dissipation. In this case a further contribution might result in thermally overcoming the energy barrier between two subsequent steps of the reaction sequence. This contribution would not change the trend of the reaction.

IV. RESULTS AND DISCUSSION

We determined the energy-optimized starting geometry of the clusters in a two-step procedure, in order to reduce the calculation time. First we calculated the energy-minimized geometry of the reconstruction on a smaller auxiliary cluster $Ga_{12}As_{14}H_{32}$ (dashed frame O in Fig. 1). While the Ga atoms are frozen, the As atoms in the top layer and in the adsorption layer (cf. Fig. 1) are allowed to move (except the As atoms on the [110] edges of the clusters) during this total energy minimization. In the second step, this optimized geometry serves as starting geometry to compose larger clusters (bold frames P and M in Fig. 1). The geometry of the larger clusters is optimized analogously by total energy minimization. These clusters represent approximately one unit cell of the $c(4\times4)$ reconstruction and are used to model the interaction with the approaching Ga atom. Point symmetrical cluster P, $Ga_{20}As_{24}H_{48}$, is used for interactions at sites A, C, D, and F; mirror symmetrical cluster M, $Ga_{20}As_{26}H_{48}$, is used for interactions at sites B, E, G, and H.

A. Energetics of single exchange or attachment processes

Using these two model clusters, we then identify the reaction pathway and transition states for the two subsequent *exchange* processes that lead to the replacement of the two As atoms of one dimer by two Ga atoms. We present here the results for dimers A-F, located at the edge of a triplet on cluster P (see Fig. 1). The results are summarized in Fig. 2, in which also the respective energies for the central dimer B-E (cluster M in Fig. 1) are introduced in brackets. The exchange reactions of incoming Ga atoms with the first and second atom of an As dimer in the adsorption layer lead to two respective sequences of metastable states (Fig. 2, I and II). During the first exchange sequence (Fig. 2, sequence I) the reaction proceeds in four stages. (a) The Ga atom reaches the surface and (b) chemisorbs into the middle of an As dimer. This configuration is similar to that predicted earlier for a Si(001) (2×1) reconstructed surface.[14] Afterwards, (c) this chemisorbed Ga atom pushes out one of the As atoms from the As dimer into a dangling state, from where (d) it desorbs from the surface. As a result of this first sequence, a Ga-As heterodimer is formed. The exchange reaction of a further Ga atom with the remaining As atom in this heterodimer is similar (Fig. 2, sequence II), however it proceeds in only three steps: (a′) just after the second Ga atom reaches the surface, (c′) it pushes out the remaining As atom into the dangling state, with (d′) subsequent desorption.

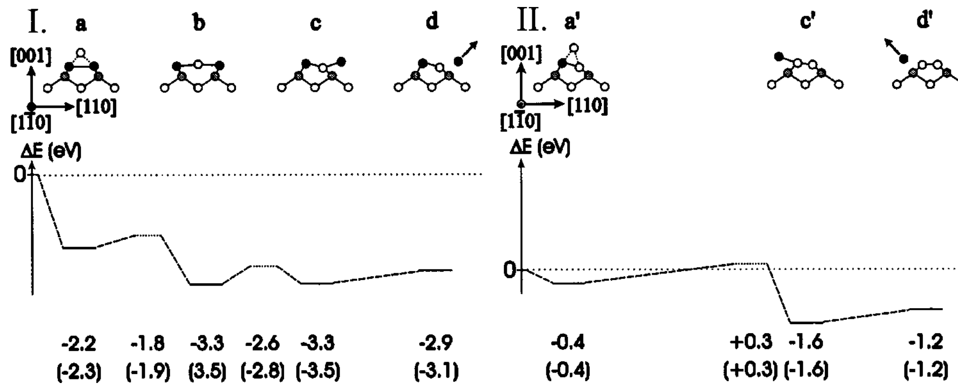


FIG. 2. Reaction pathway of two exchange processes of a Ga atom with (I) an As_2 dimer and (II) a Ga-As heterodimer. The energies of the stable conformations and transition states for dimer A-F are given below (values for dimer B-E in brackets; for definition of atom symbols, see Fig. 1).

Let us now consider the energetics of these processes (cf. the energy values given in Fig. 2). There occur three energy minima during the first exchange process (Fig. 2, I: a, b, and c). These minima show very high stability (a, -2.2 eV; b, -3.3 eV; c, -3.3 eV). The transition from a to b is characterized by a barrier of 0.4 eV. States b and c are separated by an energy barrier of about 0.7 eV and the bonding energy of the dangling As atom in the c conformation is 0.4 eV. The last barrier (position d) marks the transition to the second As exchange process in which the approaching second Ga atom expels the dangling As atom of state c. All energy values of positions with lowest local energy and of the energy barriers during the first process are negative, showing the exothermic character of this reaction. Therefore, the first As atom of the dimer can be exchanged in a continuous process. In contrast, the exchange of the second As atom (Fig. 2, II) needs to overcome in the reaction from a′ to c′ an energy barrier of 0.7 eV that reaches 0.3 eV above the zero energy level. In summary, all energies of the transition states of these exchange processes are below zero except during the exchange of the second As atom in the Ga-As heterodimer (cf. Fig. 2). It is interesting to note in this context that stable Ga-As heterodimers have recently been discovered experimentally.[5] This observation supports the notion that the barrier between a′ and c′ extending to repulsive interaction energies in fact has the significant role of causing a considerable delay in the exchange reaction course at the heterodimer state.

In the *attachment* process, an arriving Ga atom attaches to a missing-dimer site (sites G and H in Fig. 1). In this case, *no* atom is desorbed from the surface and the cluster grows by one atom. These attachment processes occur spontaneously since they are exothermic (-2.2 eV, cf. Table I, sites G and H) without being affected by energy barriers of transition states.

B. Sequence of exchange and attachment processes

Next, we compare the interaction energies for the different exchange and attachment sites and determine the most probable sequence of successive exchange and attachment processes inside a reconstruction unit cell. Here, we define the interaction energy of a sequence as the sum of the interaction energies of the individual processes. Table I summarizes the interaction energies for the various configurations of Ga atoms in the GaAs(001) $c(4\times4)$ surface. Note that there are symmetrically equivalent sites in the starting clusters (e.g., sites F and D, or A and C in cluster M). However, the Ga exchange and attachment processes break this symmetry. Only symmetrically different configurations are listed in Table I.

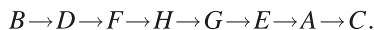
The interaction of an arriving Ga atom with the As atom in position B shows the highest energy gain, therefore the binding of the Ga atom into the middle of the three-dimer block has the highest probability compared to the occupation of one of the missing-dimer positions (G or H) or the exchange of one of the other dimer atoms (A, D, or E). The

TABLE I. Interaction energies (ΔE) of Ga atoms with the clusters that represent the $c(4\times4)$ reconstructed GaAs(001) surface. All energy values are given relative to the appropriate separated system (see the text). Negative values indicate attractive interaction. The accuracy is better than 100 meV.

Number of Ga atoms added	Considered sites[a]	ΔE (eV)
1	B	-3.1
1	D	-2.9
1	E	-3.0
1	G	-2.2
1	H	-2.2
2	BE	-3.4
2	BA	-5.6
2	BD	-5.9
2	BG	-5.2
2	GH	-4.0
3	BAC	-8.2
3	BDF	-8.8
3	BAG	-7.8
3	BAH	-7.9
4	$BDFE$	-9.8
4	$BDFH$	-10.9
4	$BDFG$	-10.8
5	$BDFHG$	-12.7
5	$BDFHE$	-11.8
6	$BDFHGE$	-13.9
7	$BDFHGEA$	-15.1
8	$BDFHGEAC$	-16.3

[a]Only symmetrically different configurations are listed. G and H are attachment sites. All others are exchange sites, where a newly arrived Ga atom replaces the As atom of a dimer.

interaction energy calculated for this step ($E=-3.1$ eV) is very close to the theoretical results of Kley *et al.* ($\Delta E=-3.2$ eV) determined on the GaAs(001) $(2\times 4)\beta 2$ surface.[15] Assuming the incorporation of the first Ga atom into position B, the next Ga atom could react with the As dimer atoms in the symmetrically different A, D, or E positions, or attach to one of the missing-dimer positions (G or H). Of these reactions, the exchange at D shows the highest energy change, therefore the highest probability. Further evaluation of the interaction energies yields the following order of the attachment (G and H) or exchange ($A-F$) processes:



$$B\rightarrow D\rightarrow F\rightarrow H\rightarrow G\rightarrow E\rightarrow A\rightarrow C.$$

We note that sites G and H have similar interaction energies (cf. Table I) and therefore their order of occupation is interchangeable within the accuracy of the calculations. These results show that during the interaction of Ga atoms with the $c(4\times 4)$ surface, first all As dimers are changed to Ga-As heterodimers, then the Ga atoms occupy the missing-dimer positions (G and H). After this configuration is formed, the Ga atoms will replace the remaining As atoms in the Ga-As heterodimers (see also Table I for energy values). However, the latter exchange processes are delayed by the repulsive energy barrier of 0.3 eV (see Fig. 2, II).

Our respective calculations show that the interaction energies listed in Table I are independent (within accuracy of the calculation) of the exchange state of the neighboring $c(4\times 4)$ unit cells. Therefore, the exchange processes can be assumed to occur independently within the different dimer triplets. This important aspect suggests that our theoretical approach can also be used to consider atomic processes on many differently reconstructed surfaces.

It is further interesting to note that the calculated sequence predicts the formation of Ga-As heterodimer triplets with a "zigzag" structure (configuration "BDF" in Table I, see Fig. 1). Experimentally, however, "straight-line" Ga-As heterodimer triplets (configuration "BAC" in Table I, see Fig. 1) dominate,[5,16] which according to our calculation are second in energy to the zigzag configuration. The reason for this discrepancy is subject to further examination.

Based on this analysis, we can visualize an idealized layer-by-layer growth process and derive within its context a formation process for As antisite defects during growth. After all As atoms are exchanged by Ga and the missing-dimer sites are occupied with Ga, the reconstruction of the surface is completely eliminated and a closed layer of Ga is formed. Now additional As atoms can form the next crystal sheet and the adsorption layer. The crystal has then grown by one GaAs monolayer and the initial surface configuration is recovered. The described growth cycle by exchange and attachment can start anew. If, however, one of the exchange steps is skipped or a desorbed As atom binds to a missing-dimer site before the next layer is formed, an As atom will remain on a Ga site, will be covered in the ongoing growth, and will then form an As antisite defect.

V. SUMMARY AND OUTLOOK

During the interaction of Ga atoms with the As-rich $c(4\times 4)$ GaAs(001) surface, the As dimers in the As adsorption layer are first turned into Ga-As heterodimers, then Ga atoms occupy the missing-dimer sites. Eventually, Ga atoms will replace the set of remaining As atoms in the Ga-As heterodimers. This latter process is hindered by an energy barrier, which can be the reason for the recently experimentally discovered stable Ga-As heterodimers. This process describes the growth of stoichiometric GaAs crystals. It, however, bears inherently a mechanism for the formation of As antisite defects that are abundant in low-temperature grown GaAs. In this case, during the formation of a complete GaAs layer some As atoms are not exchanged by Ga and remain on Ga sites.

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