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Ab initio study of atomic disorder on As-rich GaAs(111)A surface

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ABSTRACT

Mechanisms for the appearance of disorder on the As-rich GaAs(111)A surface were investigated employing density functional theory (DFT). Focus was given to the As trimer interactions by considering different surface symmetries and rest site occupations. The (2×2) and the $c(4\times2)$ structure models with As trimer and an As rest site were found the most energetically stable under the As-rich experimental conditions at $T = 0$ K. Low interactions between neighboring As trimers causes disorder in thermodynamic equilibrium at finite temperatures. A careful analysis of the configurational entropy contributions including the different statistics was carried out. The experimentally observed As-rich (2×2) structure was confirmed to be kinetically stabilized. The stabilization mechanism is discussed with respect to the As trimer migration on the surface, which is limited by a large diffusion barrier through the As rest sites.

1. Introduction

Low index group III–V semiconductor surfaces were studied in numerous publications over the last decades. Renewed interest appeared with epitaxial growth of nanostructures, including quantum dots and more recently nanowires. The knowledge of the surface structures and their energetics is essential e.g. for the determination of equilibrium shapes [1] or the basis for studying the growth dynamics [2,3].

GaAs is the protypical group III–V compound. Its clean polar surfaces exhibit a large number of surface reconstructions depending on the preparation conditions including temporal evolution of substrate temperature as well as chemical potentials of the constituents. The atomic surface structure of the GaAs(001) reconstructions was well studied [4]. The GaAs(111) surfaces, both cation terminated (111)A and anion terminated (111)B have attracted less attention, however. The GaAs(111)B surface was found to exhibit many different reconstructions depending on substrate temperature and As/Ga flux concentration ratio. A phase diagram of the GaAs(111)B surface includes the (2×2), $(1\times1)_{LT}$, $\left(\sqrt{19}\times\sqrt{19}\right)$, and $(1\times1)_{HT}$ reconstructions [5]. In contrast to the GaAs(111)B surface, only a (2×2) diffraction symmetry was reported on the cation terminated GaAs(111)A surface by reflection high-energy electron diffraction (RHEED) [5,6]. Two phases of the (2×2) structure were suggested for the GaAs(111)A surface. The Ga-rich (2×2) phase is Ga terminated and contains one Ga vacancy per surface unit cell (the vacancy buckling model, VB). This structure was confirmed by many techniques including low-energy electron diffraction (LEED) [7], grazing incidence X-ray diffraction [8], scanning tunneling microscopy (STM) [6], and *ab initio* calculations using density functional theory (DFT) [1,9–11]. The VB model was also confirmed for the InAs [12], GaSb [13], InP [14] and InSb [15,16] surfaces. The second (2×2) phase on the GaAs(111)A phase diagram is an As-rich (2×2) phase. It was suggested that this structure contains one As trimer per surface unit cell on the T_4 atomic site [1]. A similar model was suggested for the GaAs(111)B (2×2) surface [6].

Recently, the (2×2) structure of the GaSb(111)A surface was investigated by *ab initio* calculations with respect to stabilization by configurational entropy [17]. The stability of the (2×2)-VB model was confirmed for the Ga-rich conditions similar to the GaAs(111)A surface. Under more Sb-rich conditions the former (2×2) trimer model was improved by replacing the Ga atom in the second atomic layer at the rest site by Sb. A similar result was confirmed for the As-rich GaAs(111)A (2×2) surface [17]. Later, the formation process of the As-rich GaAs(111)A (2×2) phase was investigated by X-ray photoelectron spectroscopy (XPS), rocking curve RHEED, and STM measurements [18]. The As trimer with the As rest site, T(II) model in the following, was confirmed experimentally. The structure was found to be kinetically stabilized. An amorphous As film deposition and sequential substrate annealing are required to produce the As-rich (2×2) structure, whereas the As-rich structure was not obtained by cooling of the sample under constant As_2 flux. In addition, multiple phase coexistence including As trimers on top, T_4, and hollow, H_3, site positions on the surface was suggested. The agreement between the experimental and theoretical RHEED rocking curves could be achieved assuming a multiple domain structure. If the observed behavior can be understood by thermodynamic equilibrium or if kinetics is responsible can only be answered by calculating the interactions between the reconstruction domains.

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The absorption of As on the GaAs(111)A surface was studied by *ab initio* DFT calculation in the past [19,20]. The VB and As trimer models were confirmed to be stable. The absorption of As at the Ga vacancy site was found unfavorable without the presence of an As adatom or an As trimer on top of the Ga layer. The surface energy of the As adatom structure, however, was found much higher than the one of the As trimer model [10]. Atomic structure with As substitution site in the Ga layer was not considered in these studies.

In the current paper, the basic structural motifs for GaAs(111)A reconstructions are identified and their interactions are studied. The reconstruction phase diagram is extended including Bravais lattice diversity [21]. Total energy calculations are carried out on (2×2), $c(4 \times 2)$, (4×2), $\left(2\sqrt{3} \times 2\sqrt{3}\right)$ R30° [$2\sqrt{3}$ in short], and $c(4 \times 4)$ unit cells. The structural motifs include Ga vacancies, As trimers, and As or Ga rest sites within these surface unit cells. Finite temperature phase concentrations at thermodynamic equilibrium are derived by means of partition function calculations.

2. Computational details

The total energy calculations are carried out using the ABINIT computer code [22,23]. The local-density approximation for the exchange–correlation energy functional is applied. Norm-conserving pseudopotentials [24] of the Troullier–Martins type [25] are used to describe the atomic species. The electronic wave functions are expanded in a plane wave basis. A kinetic energy cutoff of 12 Hartree (Ha) and a k point set corresponding to 12×12 per (1×1) surface Brillouin zone [26] are used. Surface structures are constructed using the repeated supercell approach with slab thickness of four GaAs bilayers and trimer layer. The vacuum gap thickness of 10 Å is used. The bottom As layer of the slab is passivated by pseudohydrogens with 0.75 electronic charges. Atomic coordinates are adjusted until the interatomic forces become smaller than 10^{-4} Ha/Bohr, whereby only the three bottom layers (Ga–As–pseudo-H) are kept fixed. The surface free energy density is defined by the following expression [1]:

$$\Delta\gamma A = E_{surf} - (n_{As} - n_{Ga})\mu_{As} - n_{Ga}\mu_{GaAs}^{bulk}, \tag{1}$$

where E_{surf} represents the total energy of the system, μ_i the chemical potential of species i, n_i the number of atoms of the species i, and A is the unit cell area, respectively. The Ga-rich and As-rich experimental conditions correspond to the chemical potential range [1]:

$$\mu_{As}^{bulk} - \Delta H_f < \mu_{As} < \mu_{As}^{bulk}, \tag{2}$$

where $\Delta H_f = -0.822$ eV is the computed heat of formation of GaAs. The μ_{Ga}^{bulk} and μ_{As}^{bulk} chemical potentials are computed for the orthorhombic α-Ga [27] and rhombohedral As phases, respectively. The converged GaAs bulk lattice constant of 5.536 Å is used.

Phase concentration at an elevated temperature is estimated by the partition function calculations including the configuration entropy contributions [17]. The concentration of a phase i in thermodynamic equilibrium at finite temperature is $c_i = Z_i/Z$, $i \in S$, where Z is the partition function and S covers all possible system states, i.e. phases. In our calculations, As-rich phases with (2×2), (4×2), $c(4 \times 2)$, $2\sqrt{3}$ and $c(4 \times 4)$ unit cells are used. The partition function is expressed as follows [17]:

$$Z = \sum_i Z_i = \sum_i g_i exp\left(-\frac{\Delta\gamma_i A}{k_B T}\right), \tag{3}$$

where $\Delta\gamma_i$ is the surface energy of the i^{th} phase with area A, k_B is the Boltzmann constant, T is the temperature, and g is a degeneracy factor, which is related to the unit cell size $(m \times n)$ cells and cell symmetry. The summation is over allowed inequivalent structures. Eq. (3) is applied for unit cells with different periodicity and symmetry [17]. For larger unit cells, the product $(m \times n)$ increases, whereas the symmetry related term g changes according to the additional symmetry operations (translations, glide operation, rotations).

Adsorption–desorption behavior of As trimers on As-rich surfaces is treated by comparing the chemical potential of the solid μ_{As} with that of the molecular counterpart in the vapor phase μ_{As_2} [28–30]. μ_{As} per atom is obtained by computing desorption energy ΔE of n As atoms from the surface:

$$n\Delta E_{As} = E_{tot} - E_{ref} - n\frac{E_{As_2}}{2} \tag{4}$$

where E_{tot} is the total energy of the relaxed As-rich surface with adsorbate atoms, E_{ref} is the total energy of the relaxed structure without adsorbate atoms, and E_{As_2} is the total energy of the As_2 molecule. Gas chemical potential (per atom) is obtained by partition functions calculation [20,30]:

$$2\mu_{As_2} = -k_B T \ln\left[\frac{k_B T}{p_{As_2}} \times d\ \xi_{trans} \times \xi_{rot} \times \xi_{vib}\right] \tag{5}$$

where k_B is Boltzmann constant, T is the gas temperature, p_{As_2} is the As_2 beam equivalent pressure (BEP), $d = 1$ is the degree of degeneracy of the diatomic As_2 electron energy levels [valence electrons ground state is $(\sigma_{4s})^2\ (\sigma_{4s}^*)^2\ (\pi_{4p})^4\ (\sigma_{4p})^2$], and ξ_{trans}, ξ_{rot}, and ξ_{vib} are the molecular partition functions for the translation, vibration, and rotation motions, respectively. Partition functions are defined as:

$$\xi_{trans} = \left(2\pi m k_B T/h^2\right)^{3/2} \tag{6}$$

$$\xi_{rot} = k_B T/\sigma\overline{B} \tag{7}$$

$$\xi_{vib} = \left(1 - e^{-h\nu/k_B T}\right)^{-1} \tag{8}$$

where m is the mass of the As_2 molecule, h is Planck constant, $\sigma = 2$ is the symmetric number of As_2 molecule [29], $\overline{B} = 0.1\ cm^{-1}$ is the computed rotational constant of the As_2 molecule with As – As bond length of $r =$ 2.13 Å, and ν is the vibration frequency. As trimer adsorption–desorption diagram is derived by comparing μ_{As} with μ_{As_2}: As desorption or adsorption correspond to the $\mu_{As} > \mu_{As_2}$ or $\mu_{As} < \mu_{As_2}$ conditions, respectively.

3. Results and discussion

3.1. Ground state surface stability diagram

All structure models considered in the paper fulfill the electron counting model (ECM) [31], which is a guiding principle to evaluate stable surface reconstructions with a specific surface stoichiometry. The ECM requires that the energetically high-lying dangling bond states of the group III element (Ga) to be empty, and those dangling bond states of the group V element (As), which are lower in energy, to be filled. Hence, surfaces fulfilling ECM are likely semiconducting. In particular, a large variety of structure configurations are possible for (111)A surfaces [32]. The As-rich GaAs(111)A (2×2) models are built up from the As trimers and Ga or As rest sites. The partial electronic charges for this surface structure motifs are −3/4 and 3/4 electrons per (1×1) cell. A total electronic charge is zero for these models and, thus, these structures obey the ECM.

In the past, As trimer stacking faults on the As-rich GaAs(111)A [33,34] and GaAs(111)B [6,35] (2×2) surfaces were observed by STM. Domains with local (2×2) and $c(4 \times 2)$ periodicity were observed. A $c(4 \times 2)$ structure can be considered as a disordered (2×2) structure: two (2×2) atomic rows are shifted by one surface lattice