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Comparison of As-rich and Sb-terminated GaAs(100)(2×4) reconstructions

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Abstract

We present results of accurate first-principle total-energy calculations on Sb-terminated GaAs(100)(2×4) surfaces. We discuss the atomic structures and stability of several interface geometries in comparison with results for As-rich GaAs(100)(2×4) reconstructions. All interfaces are characterized by similar structural elements as Sb dimers with a length of about 2.9 Å, dimer vacancies and a nearly planar configuration of the three-fold coordinated second-layer Ga atoms. They are rather similar to the corresponding As-rich surface phases. In analogy to recent findings for the As-rich (2×4) surface reconstructions we favour two-Sb-dimer structures over the three-dimer model.

Keywords: Antimony; Chemisorption; Density functional calculations; Gallium arsenide; Low index single crystal surfaces; Molecular dynamics

1. Introduction

The molecular-beam-epitaxy grown GaAs(100) surface is one of the most studied polar semiconductor surfaces, because of its importance for electronic and photonic devices. A number of experimental and theoretical studies have addressed the atomic structures and energetic and electronic properties of the different reconstructions of the GaAs(100) surface [1–4]. Much less is known about the modification of the surface properties through deposition of other species. The interest in the Sb adsorption on GaAs(100) is due to the interface electronic properties [5] and to the possible use of Antimony as surfactant for metal homoepitaxial growth on GaAs(100). Photoelectron spectroscopy (PES), Auger, low- and reflection high-energy electron diffraction (LEED and RHEED, respectively) studies have shown that the Sb/GaAs(100) interface is atomically abrupt and annealing leads to the formation of an epitaxial layer of (2×4) symmetry on the GaAs(100) surface [6–8]. Maeda et al. [7] proposed a structural model for the Sb-induced reconstruction in analogy to the GaAs(100)β(2×4) structure [1,4], widely used in the past to describe As-terminated GaAs(100)(2×4) surfaces. This model, characterized by three Sb-dimers will be denoted as Model I in this work (see Fig. 1). X-ray standing wave (XSW) and angle-resolved photoelectron spectroscopy (ARPES) studies gave further evidence for the existence of Sb dimers on the surface [9]. However, conclusive results about the validity of the three-Sb-dimer model were not obtained.

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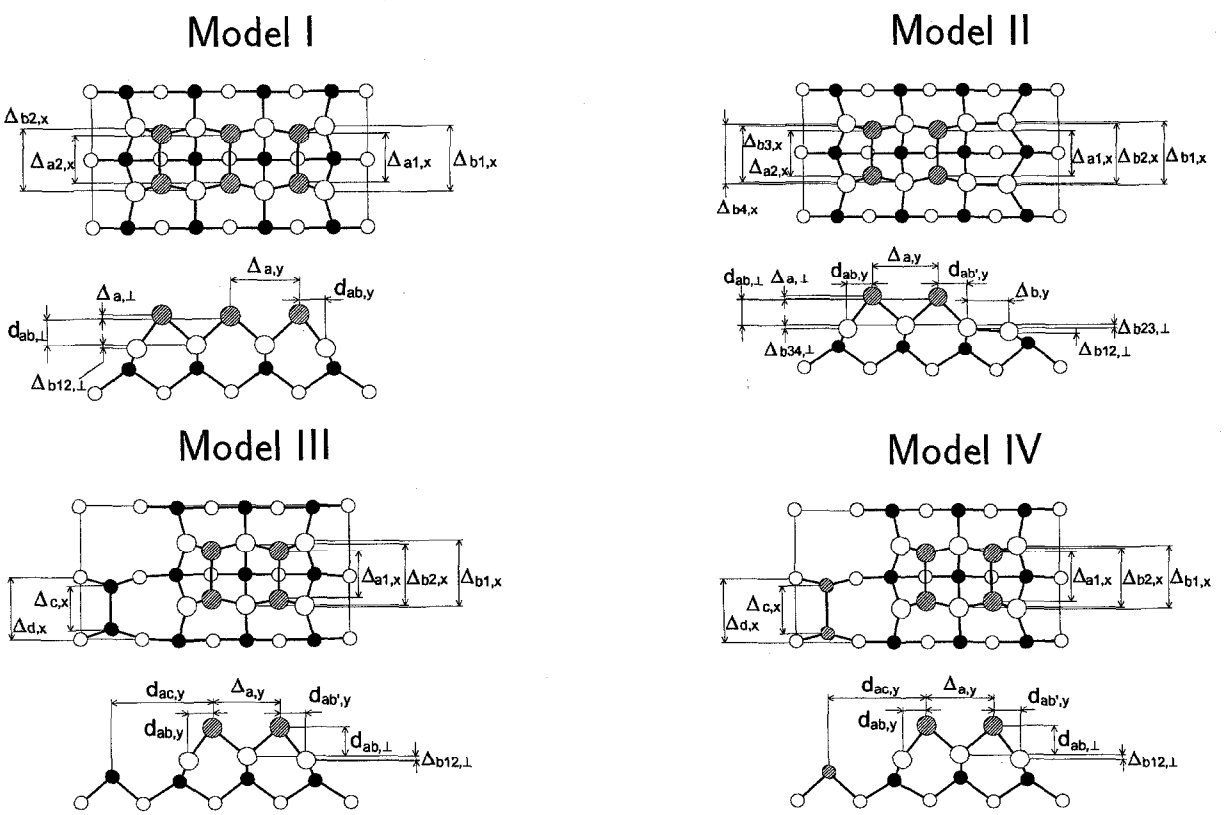

Fig. 1. Top and side view of relaxed Sb/GaAs(100)(2×4) structures. Large (small) circles indicate top and second (third and fourth) layer atoms. Substrate anions (substrate cations, antimony atoms) are denoted by full (empty, shaded) symbols.

Meanwhile, however, the majority of experimental and theoretical studies on the As-rich GaAs(100)(2×4) surface indicate that the appropriate structure to explain the reconstruction is characterized by two rather than three top-layer As-dimers. The higher Madelung energy destabilizes the three-dimer structure compared to the two-dimer structure as shown in Ref. [1]. The same argument should hold in case of the Sb-terminated GaAs(100)(2×4) surface. The three-Sb-dimer structure has also been questioned in a recent reflectance anisotropy spectroscopy (RAS) investigation [10] which indicates the coexistence of Sb and Ga dimers at the surface. Considering the present understanding of the As-terminated GaAs(100)(2×4) surface, several models as shown in Fig. 1 appear plausible to describe the adsorption geometry and will be considered in the following. We mention that all four models are consistent with electron counting heuristics.

We apply ab initio total-energy calculations to study the geometry and energetics of the Sb/GaAs(2×4) interface. Our calculations are on the same footing as a study recently published on As-rich GaAs(100)(2×4) reconstructions [4]. This allows precise comparisons and the determination of the chemical trend.

2. Method

We apply density-functional theory in local-density approximation (DFT-LDA). The surface is simulated by a periodic slab with 8 atomic (100)(2×4) layers and a vacuum region equivalent in thickness. The Ga-terminated surface of the slab is saturated with fractionally ($Z=1.25$)

charged H atoms. The two bottom layers on this side of the slab are kept frozen, whereas all other atoms are relaxed using a molecular-dynamical approach [11]. The electric field resulting from the inequivalence of the two surfaces is accounted for by applying a dipole correction to the electrostatic potential calculated self-consistently. Single-particle orbitals are expanded into plane waves up to an energy cut-off of 15 Ryd. $\boldsymbol{k}$-space integrations are replaced by a sum over four special points in the irreducible part of the surface Brillouin zone. This approach and numerical parameters have proven successful in determining precisely the structural and dynamical properties of the Sb/GaAs(110) interface [12].

3. Results

To determine the ground state geometries for the adsorption models we relaxed a series of structures with buckled and twisted dimers until the forces acting on the atoms were below 0.025 eV Å^{-1}. The minimum energy configuration of Models I and II is symmetric. For Models III and IV we observe a slight buckling of 0.03 and 0.02 Å, respectively, accompanied by a nearly vanishing twisting of the Sb-dimers. All structures are characterized by a Sb-dimer length of 2.86–2.87 Å, rather close to the experimentally determined value of 2.95 ± 0.06 Å [9]. We observe a nearly planar bonding situation of the three-fold coordinated second-layer Ga atoms. Further structural details are given in Table 1. The interface geometries are very similar to the respective α, β, and $\beta 2$ models of the As-rich surface [4]. The Sb dimers are about 14% longer and the dimer–dimer separation is about 3% larger than in case of As-rich surfaces. This is simply due to the covalent radius of Sb, which is about 17% larger than that of As. The size difference of the overlayer atoms leads also to slight changes in the layers beneath: the length of the Ga dimers found for Model II amounts to 2.46 Å, while it is 2.51 Å in case of the GaAs(100)$\alpha(2\times4)$ structure. As already observed for the As-rich surface, there is a bimodal bond length distribution between top layer anions and second layer cations. The distances between three-(four-) fold coordinated second-layer Ga atoms to the nearest Sb overlayer atom amount to 2.49–2.51 (2.59–2.66) Å for all models. The latter values are close to the GaSb bulk bond length.

Table 1
Geometrical parameters in Å of four models for relaxed Sb/GaAs(100)(2×4) structures according to Fig. 1

Sb/GaAs(100) (2×4)	Model I	Model II	Model III	Model IV
$\Delta_{a1,x}$	2.86	2.86	2.86	2.86
$\Delta_{a2,x}$	2.86	2.86	–	–
$\Delta_{b1,x}$	3.73	3.87	3.72	3.73
$\Delta_{b2,x}$	3.63	3.71	3.64	3.66
$\Delta_{b3,x}$	–	3.62	–	–
$\Delta_{b4,x}$	–	3.72	–	–
$\Delta_{c,x}$	–	–	2.52	2.87
$\Delta_{d,x}$	–	–	3.68	3.76
$\Delta_{a,y}$	3.91	4.01	3.95	3.95
$\Delta_{b,y}$	–	2.45	–	–
$d_{ab,y}$	1.47	1.57	1.46	1.45
$d_{ab',y}$	–	1.81	1.48	1.47
$d_{ac,y}$	–	–	5.94	5.93
$\Delta_{a,\perp}$	0.09	0.09	–	–
$\Delta_{b12,\perp}$	0.19	0.23	0.26	0.26
$\Delta_{b23,\perp}$	–	0.15	–	–
$\Delta_{b34,\perp}$	–	0.17	–	–
$d_{ab,\perp}$	1.68	1.64	1.74	1.74

Due to the different number of Sb and Ga atoms per surface unit cell the comparison of the surface energies of the different models has to take into account the Sb and Ga chemical potentials. Upper limits on the chemical potentials μ are set by the bulk elements [13]. In order to assess the stability we show in Fig. 2 the phase diagram of the interface in dependence of the chemical potentials of Ga and Sb in a range $-1\,\text{eV} \le \mu - \mu_{\text{bulk}} \le 0$. As result we find that in the extreme limit, where the Sb and Ga chemical potentials equal those of the respective bulk phases, Model IV is the most stable adsorption configuration. For lower values of μ(Sb) Model II, or depending on the value of μ(Ga), Model III are more favourable. Model I, proposed to describe the interface geometry in most previous studies, is unstable with respect to Model IV independent of the assumed chemical potentials. Its energy difference to Model IV is 0.03 eV per (1×1) surface unit cell. This difference roughly equals that found between the β and $\beta 2$

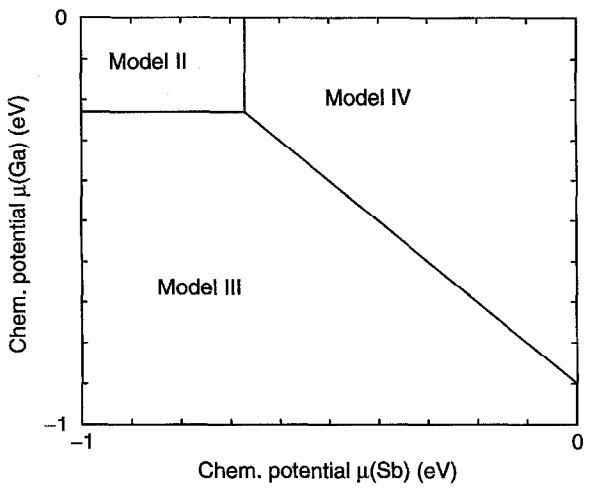

Fig. 2. Phase diagram of the Sb/GaAs(100)(2×4) interface versus the Sb and Ga chemical potentials in the respective range of $-1\ \text{eV} \le \mu - \mu_{\text{bulk}} \le 0$. Model I is no equilibrium structure, independent of the Sb and Ga chemical potentials.

reconstruction of the clean GaAs(100)(2×4) surface [1,4].

Solely on grounds of energy arguments we cannot discriminate between the remaining three adsorption models. However, the existing experimental findings allow some speculation. The preparation of the Sb–GaAs(100)(2×4) reconstruction requires an annealing at 500–560°C [7,8,10]. Already at lower temperatures the $\beta 2 \rightarrow \alpha$ phase transition takes place at As-rich GaAs(100) surfaces(see, e.g., Ref. [2]). In analogy, one can expect that the high annealing temperature, which causes a Ga-rich and As- and Sb-poor environment favours the α-like Model II. This is also in agreement with a recent RAS study [10], which indicates the coexistence of Sb and Ga dimers at the interface.

4. Conclusions

We have performed total-energy calculations on a series of adsorption models for the Sb/GaAs(100)(2×4) interface. We find the atomic structures of the interfaces to be very similar to those of As-terminated GaAs(2×4) reconstructions. Remaining differences are due to the larger size of the overlayer anions. The analogy between As-rich and Sb-terminated surfaces holds also for the energetic ordering of the surface structures. The three-Sb-dimer model widely used in the past to explain the interface geometry is out of range of the energetically stable structures. The calculated phase diagram in conjunction with the experimental findings indicates a interface structure characterized by two top-layer Sb dimers and a dimerization of the exposed second-layer Ga atoms.

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