AB INITIO CALCULATION OF THE ATOMIC AND ELECTRONIC STRUCTURE FOR Sb ADSORBED ON GaAs(110) *)

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We report results obtained by a systematic study of Sb adsorption on the relaxed GaAs(110) surface, using density-functional theory within the local-density approximation (LDA) and norm-conserving, fully separable, ab-initio pseudopotentials. The GaAs(110) surface is simulated by a slab geometry wherein the atomic structure of the Sb atoms at the preferred adsorption positions and the uppermost substrate layer is optimized by minimizing the total energy, in contrast to previously reported theoretical approaches obtaining the surface bandstructure for given geometrical equilibrium structures. Sb coverages of $\Theta = 1/2$ and $\Theta = 1$ are considered. We give a detailed analysis of the total-energy surface of the Sb/GaAs(110) system and identify stable and metastable adsorption sites. The resulting equilibrium geometries are discussed: We interpret these results in terms of the Sb-Sb interaction within the chains parallel to the $[1\bar{1}1]$ direction and of possible structural instabilities in such chains. The atomic positions are compared with results of LEED analysis, stating an overall agreement except the buckling of the chain atoms. The resulting electronic properties (surface bandstructure, photothreshold, Schottky barrier) are discussed within the context of experimental data available from STM, photoemission spectroscopy, etc.

The determination of the atomic structure of overlayers adsorbed on compound semiconductors is an important step towards understanding the mechanism of Schottky barrier formation and growth of multilayer heterojunction systems. One of the more extensively studied systems is Sb on GaAs(110). Room-temperature deposition of one monolayer ($\Theta = 1$) of Sb on GaAs(110) has been found to result in a stable and ordered 1×1 adsorbate structure. However, experimental results do not give a clear idea about the atomic structure of this system. Based on photoemission and low-energy electron diffraction (LEED) studies, Skeath et al. [1] proposed two different atomic structures — the "epitaxial continued layer structure" (ECLS) and the "p^3" structure. Duke et al. [2] examined five qualitatively distinct classes of geometrical models — the ECLS, the "p^3" structure, the "epitaxial overlapping chain structure" (EOCS), a dimer model, and a defect model ($\Theta = 1/2$). Their LEED analysis favours the ECLS over the others.

The aim of the present study is to apply accurate self-consistent total-energy calculations to determine the preferred adsorption sites of Sb on GaAs(110). Basing on the results for one adatom per pair of Ga and As atoms on the surface ($\Theta = 1/2$),

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we compare five structures for $\Theta = 1$. Their atomic positions are allowed to relax, and the total energies are calculated at the equilibrium atomic structure.

We perform parameter-free electronic structure, total-energy, and force calculations based on the density-functional theory (DFT). The electron-ion interaction is treated by using norm-conserving, *ab initio*, fully separable pseudopotentials in the Kleinman-Bylander form [3] as given in Ref. [4], and the many-body electron-electron interaction is treated within the local-density approximation (LDA) and the Ceperley-Alder scheme [5] as parametrized by Perdew and Zunger [6]. We use the repeated-slab method to simulate the semiconductor surface. The slab contains eight layers of GaAs(110), both sides covered with Sb, and a vacuum region equivalent in thickness to six of such layers. An energy cutoff of 8 Ry is used for the plane-wave basis set, which corresponds to about 1500 plane waves for the 1×1 systems. To make sure that the results are well converged, some results are checked by using a cutoff of 18 Ry, corresponding to more than 5000 plane waves. The $\boldsymbol{k}_{\parallel}$-integration is replaced by a sum of four special $\boldsymbol{k}_{\parallel}$ points in the irreducible part of the surface Brillouin zone. In order to determine the equilibrium atomic positions, the atoms of the three outermost substrate layers and the adatoms are relaxed to geometries given by the calculated total energy and forces, using a steepest-descent method for the atomic displacements together with a Car-Parrinello-like approach [7] for bringing the wave functions to self-consistency.

Proceeding from the mentioned structural models for the monolayer coverage, we find that there are at least five local minima in the total-energy surface corresponding to different atomic geometries. However, one should take into account that these minima are obtained under the constraint of symmetry. The structural parameters of these geometries are given in Table 1. The obtained structures are in qualitatively good agreement with the predictions of Duke et al. [2] except the found counterrelaxation of the outermost GaAs layer for the p^3 structure, possibly induced by a change in the character of the bonding. The ECLS model, considered theoretically in detail in Refs. [11,12] is clearly the structure of choice. The epitaxial on-top structure (EOTS) which better fits to the STM images [13] is at least at zero temperature 0.25 eV higher in energy. Furthermore, it is striking that the structures which nearly preserve the covalent radii are much deeper in energy than the EOCS and the Sb_2-dimer, respectively. Apart from the EOCS, all the structures show the same Sb-Sb bond length of about 2.8 Å, indicating a strong covalent bonding between the adatoms. Moreover, the geometrical parameters of the ECLS may be compared with those obtained by LEED [8], and the agreement both of the theoretical and experimental data also establishes the ECLS to be the most probable geometry.

The self-consistent potentials obtained during the calculation allow to determine the barrier seen by an electron passing from the bulk to the vaccuum region. The photothreshold corresponds to the difference between this potential barrier and the valance band maximum. For the relaxed GaAs(110) surface and the three Sb/GaAs(110)-(1ML) systems lowest in energy, we got the following results: GaAs(110): 5.5 eV, ECLS: 5.0 eV, EOTS: 4.8 eV, and p^3-structure: 4.4 eV.

Table 1. Structural parameters in Å for the geometries of the GaAs(110)-Sb(1ML) system. The present results (obtained for 8/18 Ry cutoff energy) are compared with the results of the LEED analysis by Ford et al. [8], the tight-binding results of LaFemina et al. [9], and *ab initio* pseudopotential calculations by Srivastava [10].

	ECLS	p^3 structure	EOTS	EOCS	dimer model
Present results $\Delta_{1,\perp}$	0.05/0.06	0.70	0.15	0.08	1.25
LEED [8]	0.08				
tight-binding [9]	0.04		0.33	0.13	
ab initio [10]	0.04				
present results $\Delta_{1,y}$	2.00/2.00	1.94	2.04	2.28	2.52
LEED [8]	1.99				
tight-binding [9]	1.86		1.83	2.11	
ab initio [10]	1.91				
present results $d_{12,\perp}$	2.35/2.36	2.89	2.73	2.43	2.76
tight-binding [9]	2.35		2.93	2.11	
present results $d_{12,y}$	4.51/4.50	0.52	1.41	1.41	5.56
tight-binding [9]	4.47		1.25	1.74	
present results $\Delta_{2,\perp}$	0.08/0.10	0.23	0.03	0.04	0.06
LEED [8]	0.11				
tight-binding [9]	0.03		0.27	0.16	
ab initio [10]	0.09				
present results $\Delta_{2,y}$	1.38/1.40	1.37	1.36	1.50	2.74
LEED [8]	1.40				
tight-binding [9]	1.41		1.32	1.69	
ab initio [10]	1.43				
present results $d_{23,\perp}$	1.96/2.00	1.73	1.95	1.96	2.00
present results $d_{23,y}$	2.71/2.70	2.76	2.71	2.80	2.76

In Fig. 1 we show the total-energy surface obtained for the 1×1 half-monolayer case. Note that this total-energy surface shows a deep channel which is quite rectilinear and parallel to the [$\bar{1}$10] direction. The absence of minima localized in front of the As and Ga atoms, respectively, is somewhat unexpected. We find instead two equivalent energy minima in between the As and the two opposite Ga atoms. The atomic structure at minimum position is characterized by a small counterrelaxation of the outermost substrate layer of about 0.07 Å and a lateral displacement of the As towards the Sb atom of about 0.22 Å. This displacement of the As atom results in different bond lengths of the two neighbouring Ga atoms to the As atom. The Sb atom is there in a bridge site position and bound both to the As and to the Ga atom. As one should expect from the electronegativities, the bonding charge is closer to the Sb and As sites, respectively, than to the Ga site. The two minima within the surface unit cell are separated only by small barriers of 0.2 eV in front of the As site and 0.3 eV in front of the Ga site. The existence of

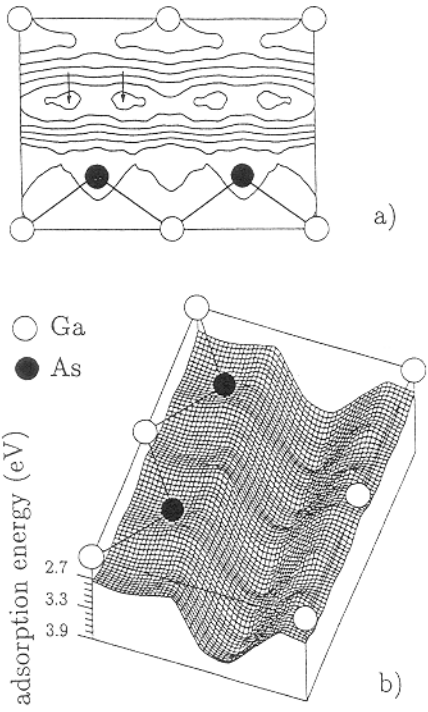

Fig. 1. Total-energy surface of the GaAs(110)-p(1 × 1)-Sb(1/2 ML) system drawn over an area of two surface unit cells (a) as contour plot and (b) in a three-dimensional perspective view. There are two equivalent quite flat minima per unit cell (indicated by arrows) in between the As atoms and the two opposite Ga atoms.

such two energetically equivalent minima causes a broken symmetry for the 1 × 1 coverage $\Theta = 1/2$, possibly giving an explanation of failing to find an ordered 1 × 1 structure of this coverage up to now. The relatively high adsorption energy of about 2.7 eV even on the plateau of the energy surface on top of the Ga-As chain arises partially from a weak interaction between the Sb atom even at the distance of 3.9 Å.

For a more detailed discussion of the half-monolayer coverage, overlayer systems with larger than 1 × 1 surface unit cells should be considered. A 2 × 1 zig-zag chain structure turns out to be more favoured in energy by about 0.4 eV per Sb atom than the 1 × 1 system for $\Theta = 1/2$. Its geometrical data indicate a considerable buckling both within the Sb-Sb chains and the top GaAs layer. Note that the buckling within the Sb-Sb chains (parameter $\Delta_{1,\perp}$) is opposite to that of all the considered 1 × 1 monolayer systems (cf. Table 1). The Sb-Sb bond length is nearly the same as in the energetically most favoured 1 × 1 systems for $\Theta = 1$ (about 2.8 Å).

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