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Energetics and Structure of Ordered Sb Overlayers and Sb Clusters on GaAs(110) Probed by *Ab Initio* Calculations.

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Abstract. – *Ab initio* density-functional theory calculations of Sb-covered GaAs(110) surfaces are performed for different coverages, different 2D translational symmetries, and various structural models. The highest adsorption energy is found for monolayer coverage ($\Theta = 1$), 1×1 translational symmetry, and the epitaxial continued layer structure. The energy gains for similar structures in the submonolayer case with lower translational symmetry are slightly smaller. Our results indicate a tendency for the formation of anisotropic islands for $\Theta < 1$ growing together in an ordered overlayer for $\Theta = 1$.

The interfaces formed when semi-metals are deposited onto atomically clean surfaces of III-V compound semiconductors have attracted considerable interest. In several aspects the Sb/GaAs(110) system has been the prototypical interface. For submonolayer coverage, Sb films form two-dimensional terraces on the surface, separated by regions of clean GaAs. When the surface is covered with one monolayer (1 ML), *i.e.* two Sb atoms per GaAs(110) 1×1 unit cell, the Sb islands grow together and form an ordered 1×1 overlayer [1]. There results a stable, well-ordered, unreactive, and non-disruptive interface between the overlayer and the substrate. Due to its unique structure the monolayer Sb/GaAs(110) interface has been considered as a model system to study the Schottky-barrier formation at metal/III-V semiconductor interfaces [1-3] experimentally and theoretically.

Although there have been numerous studies of Sb film formation on GaAs(110), the basic mechanisms involved are not well understood. Factors that affect nucleation, subsequent island growth, and finally the formation of 1 ML overlayers—such as the magnitude of interactions between adsorbate and substrate atoms, its dependence on coverage, and surface atom diffusion—are not clarified [1]. There is still no clear connection between structural and electronic properties. Because of the difficulties for experimental and theoretical studies in the submonolayer regime, the lack of information about the adsorption is rather understandable. Nevertheless, there is also an ongoing debate concerning the structural models and the details of the interface geometry in the 1 ML case [1, 4-6]. These aspects are crucial for a better understanding of the Schottky-barrier formation and the nature of the electronic states responsible for the Fermi-level pinning [1-3].

In this letter, we report results of parameter-free density-functional theory (DFT)

calculations addressing the above-mentioned energetical and bonding aspects as well as the resulting geometrical structures and accompanying electronic states. We study nine different structural models representing monolayer and submonolayer Sb overlayers. We show that from the energetical point of view the 1×1 structure, where the Sb adatoms occupy positions similar to what would be the atomic positions of Ga-As zig-zag chains at an unrelaxed GaAs(110) surface, is the most favourable one. Similar submonolayer structures, where, however, Sb-Sb chains are missing and, hence, the translational symmetry is reduced, give rise to slightly smaller adsorption energies. The formation of islands with local 1×1 symmetry seems to be more favourable than a structure with a more or less homogeneous Sb distribution but lower translational symmetry.

Our conclusions are drawn from *ab initio* total-energy and electronic-structure calculations based on the density-functional theory (DFT) and applying the local-density approximation (LDA) for the exchange correlation functional [7]. The electron-ion interactions are treated by norm-conserving, *ab initio*, fully separable pseudopotentials [8]. 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 atomic layers. An energy cut-off of 8 rydberg is used for the plane-wave basis set. To make sure that the results are well converged, some results are checked with a cut-off of 18 rydberg. The $\boldsymbol{k}_{\parallel}$-integration is replaced by a sum over four special $\boldsymbol{k}_{\parallel}$ points in the irreducible part of the surface Brillouin zone. In order to determine the equilibrium positions, the atoms of the three outermost substrate layers and the adatoms are relaxed to geometries until the total energy and the forces are minimized. We use a steepest-descent method to displace the atoms together with a Car-Parrinello–like approach [9] for bringing the wave functions to self-consistency. The computer code cp93fhi of Stumpf and Scheffler [10] is applied.

In order to describe the atomic geometry of the stable and well-ordered 1×1 1 ML Sb adsorbate on GaAs(110), five structural models are discussed. Besides the widely supposed «epitaxial continued layer structure» (ECLS) a «p^3 structure», an «epitaxial on-top structure» (EOTS), an «epitaxial overlapping chain structure» (EOCS), and a «dimer structure» are considered [1, 4, 5]. Each structure gives rise to a local minimum in the total-energy surface, *i.e.* each structure represents a stable or metastable geometry for low temperatures. The adsorption energies per Sb atom vary between 4.48 eV (ECLS) and 3.43 eV (EOCS) (cf. table I). Although the adsorption energies are overestimated by about

TABLE I. – *Adsorption energies per* Sb *adatom and bond lengths in the first two atomic layers for monolayer* Sb/GaAs(110) 1×1 *systems. The shortest bond length is taken, if more than one distance comes into question. The second values for* ECLS *result from a calculation with the energy cut-off of* 18 Ry.

Geometry models	Adsorption energy (eV)	Bond length (Å)			
		Sb-Sb	Ga-Sb	Sb-As	Ga-As
ECLS	4.48/4.42	2.79/2.79	2.55/2.57	2.64/2.64	2.39/2.40
p^3 structure	4.13	2.83	2.61	2.79	2.39
EOTS	4.23	2.82	2.67	2.77	2.38
EOCS	3.43	3.00	2.81	3.14	2.46
dimer structure	3.55	2.81	2.76	2.96	2.43

0.5 eV per bond by the DFT-LDA method [11] (1), their differences are of high accuracy and can therefore be used to discriminate structures. From the energetical point of view the ECLS model is clearly the structure of choice, in rather complete agreement with I EED and X-ray standing-wave (XSW) studies [5, 6] and theoretical considerations within the tight-binding (TB) method [4, 12] and other DFT-LDA calculations [13, 14]. The EOTS model, which perhaps better fits to the STM images [4], as well as the p^3 structure, are only 0.25 or 0.35 eV higher in energy. On the other hand, the EOCS and dimer models seem to completely fail.

The different adsorption energies of Sb can be related to its bonding behaviour and to the different substrate structures, *i.e.* counterrelaxation or relaxation. Each Sb atom forms three strong and highly directional bonds, one to the substrate (Ga or As) and two to the neighbouring chain atoms, only in the ECLS and EOTS cases. Although twisted by 180°, in both geometries Sb-Sb zig-zig chains appear parallel to the $[\bar{1}10]$ direction. In the first case, the Sb positions follow from a continuation of the nearly unrelaxed GaAs substrate, whereas for the EOTS the Sb adatoms sit nearly on top of Ga and As, respectively. As can be seen from table I, these structures nearly conserve the bond length close to the sum of covalent radii of 2.80 Å (Sb-Sb), 2.66 Å (Ga-Sb), 2.60 Å (Sb-As), and 2.46 Å (Ga-As). The shorter adsorbate-substrate bond lengths probably explain why the ECLS is lower in energy than the EOTS. The EOCS and the dimer model completely fail this test. The energetical failure of the p^3 structure follows from the fact that in this case Sb p-orbitals and near As p^3-hybrids cannot form a strong bond.

More indirect information about the validity ofa certain structural model arises also from electronic-structure calculations. Therefore, we compare the resulting surface bands with band-mapping results of angle-resolved–photoemission (ARPES) [15, 16] and inverse-photoemission [17] spectroscopy. The dimer structure, the EOCS, the EOTS, and the p^3 model fail this test. The first two structures give rise to metallic interfaces. The reasonable agreement of the occupied interface bands resulting within ECLS are indicated in fig. 1. The dispersion of the nearly degenerated S_3 and S_4 bands can be perfectly reproduced. However, also the most important measured features near the top of the occupied states can be explained by the bands S_5, S_6 and A_2. The overall agreement seems to be better as in the case of previous DFT-LDA band structure calculations [18]. We trace back this fact to the use of a geometry optimized by *ab initio* total-energy calculations, whereas ref. [18] uses a structure derived from LEED analyses [5], and of an exchange-correlation potential beyond the X_α approximation.

Practically nothing is known about the bonding behaviour of the Sb atoms in the submonolayer case. This holds also for the preferential adsorption positions and the modification of the GaAs(110) surface geometry in the atomic limit of the coverage. In order to get an idea about the behaviour of an Sb adatom on GaAs(110) 1×1 we have evaluated the Born-Oppenheimer total-energy surface of a surface Sb atom. For more than thirty antimony positions within the two-dimensional surface unit cell, the adsorbate-substrate distance, as well as the Ga and As positions in the top three layers, were fully relaxed. In fig. 2 we show the resulting total-energy surface for the half-monolayer (1/2 ML) case, *i.e.* one antimony atom per surface pair of Ga and As. The most pronounced feature of the energy surface is the deep channel which is quite rectilinear and parallel to the $[\bar{1}10]$ direction, *i.e.* the direction of the Ga-As zig-zag chains. The absence of minima localized in front of the Ga and As dangling bonds, respectively, is somewhat unexpected. In the case of sodium on GaAs(110) such

(1) The computed value for the cohesive energy per bond is 2.05 eV (2.00 eV) for bulk GaAs (GaSb) and a cut-off of 18 Rydberg, whereas the corresponding experimental energy amounts to 1.63 eV (1.48 eV).

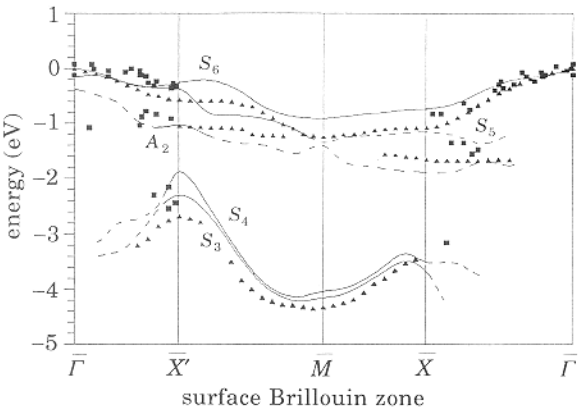

Fig. 1.

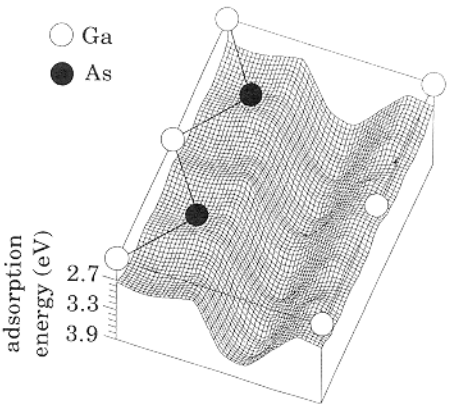

Fig. 2.

Fig. 1. – Comparison of the dispersion of interface bands for 1 ML Sb/GaAs(110) 1×1, computed for the ECLS, with ARPES values of ref. [15] (squares) and ref. [16] (triangles).

Fig. 2. – Total-energy surface of the 1/2 ML Sb/GaAs(110) 1×1 system plotted *vs.* an area of two GaAs(110) surface unit cells as a three-dimensional perspective view. For a clear presentation the surface Ga-As zig-zag chains are indicated.

minima have been found actually [19]. We relate these findings to the simpler electronic structure of the alkali atoms. Because of the five valence electrons, Sb tends to adsorption sites with higher coordination. Indeed, we find two flat equivalent energy minima within the deep channel in between one As (Ga) atom and the two opposite Ga (As) atoms from the neighboured zig-zag chains indicating long-bridge-bond adsorption positions.

Two important conclusions follow from the particular shape of the energy surface in fig. 2. The existence of two energetically equivalent minima may cause a symmetry break leading to a lowering of surface translational symmetry, *i.e.* reconstruction, or even destroying of the translational symmetry, *i.e.* clustering. This conclusion is supported by the relatively small adsorption energy of 3.89 eV in comparison with the corresponding value of 4.48 eV for the full monolayer coverage (ECLS model), which makes other structures more favourable from the energetical point of view. The energy surface in fig. 2 exhibits no indication for a preferential adsorption site. Apart from experimental complications due to the large size of the Sb islands even for low coverages, this finding may enlight different interpretations concerning a preferential bonding of Sb atoms to Ga sites [20] or not [1].

The particular form of the energy surface in fig. 2 indicates a highly anisotropic diffusion of the Sb atoms at the GaAs(110) surface. The variation of the total energy along the $[\bar{1}10]$ channel is small. The equivalent minima are separated by barriers $E_{\parallel}$ of 0.18 eV (0.35 eV) on connection lines between two As (Ga) atoms in [001] direction. The energy barriers $E_{\perp}$ perpendicular to the channel are calculated to be about 1.2 eV. Since the energy barriers strongly modify the temperature dependence of the diffusion coefficient $D \sim \exp[-E_{\parallel,\perp}/k_B T]$, one expects widely different diffusion lengths parallel and perpendicular to the channel. We believe that these findings can be an explanation of the STM observations [1] that at submonolayer coverage the Sb atoms form ordered islands along the zig-zag chains of cations and anions in the $[\bar{1}10]$ direction.

Based upon the results of fig. 2, we have additionally studied three 2×1 or 1×2 reconstructed Sb/GaAs(110) surfaces for the half-monolayer coverage in more detail. The

TABLE II. – *Structural parameters in* Å *of* Sb/GaAs(110) *structures favoured for* 1 ML (1 × 1 ECLS) *and* 1/2 ML (2 × 1 *missing-chain structure*).

	ECLS (1 ML)	Missing-chain structure (1/2 ML)
$\Delta_{1,\perp}$	0.05	− 0.14
$\Delta_{1,y}$	2.00	1.97
$\Delta_{2,\perp}^{(i)}$	− 0.08	0.42 0.18
$\Delta_{2,y}^{(i)}$	1.38	1.22 1.32
$d_{12,\perp}$	2.35	2.68

three structures considered consist of Sb chains of different form, orientation and Sb-Sb bond length. One geometry is a missing-chain structure. It represents an ECLS model where every second Sb-Sb zig-zag chain parallel to the [$\bar{1}$10] direction is missing. Linear chains of Sb atoms grown in [001] direction on top of every second row of Ga atoms are assumed in the second model. Zig-zag chains parallel to the [001] direction with Sb adatoms bonded to the Ga and As dangling bonds are the structural elements of the third model. The adsorption energies per Sb atom resulting for the three structures are 4.25 eV, 3.46 eV, and 3.83 eV. That means the 2 × 1 missing-chain structure turns out to be remarkably more favoured from the energetical point of view over the two 1 × 2 structures under consideration. However, this holds also with respect to the 1 × 1 structure studied for the same coverage 1/2 ML in fig. 2. The energy gain compared with this 1 × 1 long-bridge-bond geometry is about 0.4 eV. As in the 1 ML case, these findings indicate the central role of the strong and directional bonds of Sb adatoms with the substrate and between each other also for submonolayer coverage.

In conclusion, comparing the 2 × 1 structure and the 1 × 1 geometry, we find the energetical favouring of an inhomogeneous coverage *vs.* the homogeneous distribution of the adatoms in the submonolayer case, at least for 1/2 ML. This can again be interpreted as a physical reason for a tendency towards the formation of flat clusters. The break of the adatom overlayer parallel to the chains in [$\bar{1}$10] direction does not give rise to a substantial loss of adsorption energy. However, the adsorption energy for the ECLS (1 ML) is slightly larger than that for the missing-chain structure (1/2 ML). This fact results from slightly differently relaxed surface geometries and the vanishing interaction of second-nearest-neighbour zig-zag Sb-Sb chains parallel to the [$\bar{1}$10] direction. Their distance in [001] direction amounts nearly to 5.5 Å within the ECLS. This can be identified as the physical reason for the formation of flat islands with local 1 × 1 symmetry and local 1 ML coverage as observed experimentally [1].

Nevertheless, based upon the slight energy difference but without taking into account boundary effects, a clear discrimination of the 2 × 1 missing-chain structure cannot be stated. Therefore, several key structural parameters for the 1 × 1 ECLS (1 ML) and 2 × 1 missing-chain structure (1/2 ML) are given in table II. We consider the buckling amplitudes $\Delta_{1,\perp}$ in the first Sb layer and $\Delta_{2,\perp}^{(i)}$ in the second GaAs layer. The perpendicular extents of the zig-zag chains in the (110) planes are $\Delta_{1,y}$ and $\Delta_{2,y}^{(i)}$. Additionally the characteristic vertical distance $d_{12,\perp}$ of first and second layer is given. The index $i = 1, 2$ indicates GaAs pairs covered with Sb ($i = 1$) or not ($i = 2$). Despite the similarities in the energetics and the appearance of chains, there are two essential discrepancies in the structures. Whereas in the

monolayer case the relaxation of the GaAs surface layer is completely lifted and even a small counterrelaxation appears, the GaAs(110) surface remains relaxed for a coverage of 1/2 ML. Of course, the buckling parameters $\Delta_{2,\perp}^{(i)}$ are somewhat smaller than the value of about 0.6 Å for the clean surface and depend on the coverage itself. The buckling $\Delta_{1,\perp}$ in the Sb chains follows more or less the movement of the substrate atoms to which the adatoms are bonded. As a result, the average distance overlayer-substrate is somewhat increased in the half-monolayer case.

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