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Coverage-dependent bonding of Sb on GaAs(110)

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Abstract

We performed total-energy pseudopotential calculations for a variety of structures for Sb adsorbed on the GaAs(110) surface. Sb coverages of $\theta = 1$ and $\theta = \frac{1}{2}$ are considered. For $\theta = 1$ we investigate five earlier proposed structures and find the *epitaxial continued layer structure* (ECLS) to be the lowest one in energy. The *epitaxial on top structure* (EOTS) which fits better to recent STM images is slightly higher in energy. The electronic structure and the changes of the ionization energies for these models are also discussed in the context of experimental results and give further evidence for the ECLS. Its structural parameters are found to be in excellent agreement both with LEED and XSW data. For a coverage of $\theta = \frac{1}{2}$ we find two equivalent minima in the total-energy surface corresponding to long-bridge positions in the 1×1 surface unit cell. Studies of 1×2 and 2×1 reconstructions for this coverage are performed as well. Together with the energetical results for $\theta = 1$ they indicate the tendency of Sb to form two-dimensional clusters for low coverages as observed experimentally.

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). Antimony strongly binds to the (110) surface of GaAs. In the submonolayer regime ($\theta < 1$) the adatoms tend to cluster together, forming islands [1–3] with a 1×1 unit cell matching that of the clean GaAs(110). These islands have a height of 2.5–2.8 Å and merge together when the coverage is increased. At the completion of one monolayer (1 ML), i.e., two Sb atoms per GaAs surface pair ($\theta = 1$), a well ordered and stable 1×1 adsorbate structure results, at least after annealing. However, experimental results do not give a clear idea about the atomic structure of this system. Five structural models [4–6] have been suggested for the 1 ML Sb coverage in order to explain the experimental data. Top views of the five structures are given in Fig. 1. Based on photoemission and low-energy electron diffraction (LEED) studies, Skeath et al. [4] proposed two different atomic structures – the *epitaxial continued layer structure* (ECLS) and the p^3 structure, corresponding to a nearly sp^3 hybridization and to a structure by which every other Sb atom is bound to the underlying Ga atom donating two electrons in its empty p_z orbital, respectively. Duke et al. [5] 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 ($\theta = \frac{1}{2}$). Their LEED analysis favours the ECLS. For this structure tight-binding [7] and pseudopotential [8]

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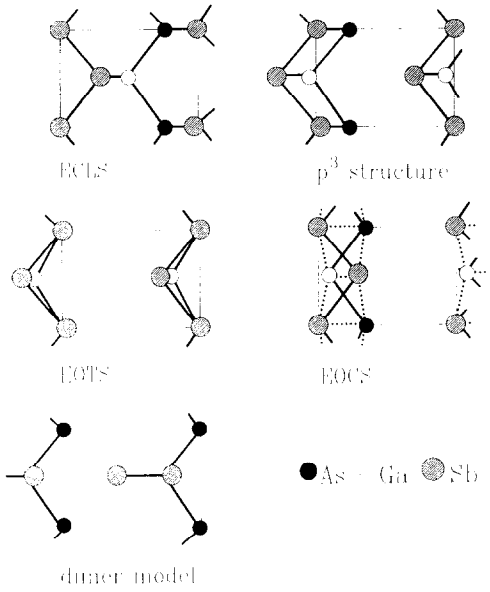

Fig. 1. Top view of different structures for 1 ML coverage of Sb on GaAs(110). The notation of atoms is valid throughout the paper.

calculations using the LEED geometry already exist. More recently LaFemina et al. [6] – using a slightly modified tight-binding scheme – have shown that the total energies of the ECLS and the *epitaxial on top structure* (EOTS), by which the Sb atoms are located nearly on top of Ga and As, are comparable within the accuracy of the used method. Furthermore they found the EOCS to be substantially lower in energy. This is in contrast to STM measurements [3], which seem to be compatible with both the ECLS and the p^3 structure but not with the EOCS or a dimer model. As pointed out by LaFemina et al. [6] the EOTS best fits to these STM images. In total-energy pseudopotential calculations the geometry for the ECLS has been optimized in excellent agreement to recent LEED measurements [9] and it was shown that the ECLS is energetically more favourable than the p^3 structure [10,11] and the EOTS [11].

In this paper these five structural models for the 1 ML Sb coverage on GaAs as well as four models concerning the submonolayer coverage are studied by means of accurate parameter-free density-functional theory (DFT) calculations. The electron–ion interaction is treated by using norm-conserving, ab initio, fully separable pseudopotentials [12]. The exchange-correlation functional of the electron–electron interaction is treated within the local-density approximation(LDA) and the Ceperley–Alder scheme [13,14]. 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 cut-off of 8 Ry is used for the plane-wave basis set. The calculation for the ECLS was done with a cut-off of 18 Ry as well in order to check the accuracy of the results. The $\boldsymbol{k}$-space integration is replaced by a sum over four special points [15]. The adatoms and the atoms of the three outermost substrat layers are relaxed until the total energy is minimized to determine their equilibrium positions. We use a steepest-descent method for the atomic displacements together with a Car–Parinello-like approach [16] for bringing the wave functions to self-consistency. Finally, we evaluate the adsorption energies and the bandstructures related to the optimized geometries.

The five structural models mentioned above for the 1 ML Sb coverage give rise to local minima in the total-energy surface. Although constraint of symmetry is assumed, these minima indicate the stability or metastability of the structures under consideration. The resulting adsorption energies per Sb atom are 4.48 (ECLS), 4.13 (p^3), 4.23 (EOTS), 3.43 (EOCS), and 3.55 eV (dimer). The adsorption energies are overestimated by the method. In the bulk case we find for instance cohesive energies per bond of 2.05 (GaAs) and 2.00 eV (GaSb), whereas the experimental values amount 1.63 and 1.48 eV. Nethertheless, their differences are of high accuracy and may therefore be used to discriminate structures. From the energetical point of view the ECLS geometry is clear the structure of choice. However, the EOTS model and the p^3 structure are only 0.25 or 0.35 eV higher in energy. The EOCS model and the dimer model fail obviously with respect to the adsorption energies. These energetical findings can be related to the bonding behaviour of the structures in ques-

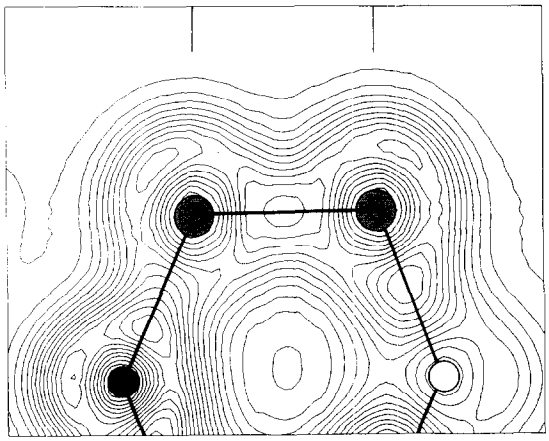

Fig. 2. Contour plots of the valence pseudo-charge density for the $\theta = 1$ adsorption of Sb on GaAs(110) in the ECLS. The plots are drawn along the three planes perpendicular to the surface containing the As–Sb, Sb–Sb, and Sb–Ga bonds as indicated by the lines in the upper part of the drawings. The contour step is 0.005 bohr^{-3}.

tion. Apart from the EOCS, which exhibits an Sb–Sb bond length of 3.0 Å, the corresponding distance for the other structures is with $d_{Sb-Sb} \approx$ 2.8 Å equal to twice the covalent radii, indicating strong covalent bonds within the Sb chains. The favoured models are also characterized by strong and directional bonds between adsorbate and substrate atoms. For the ECLS the pseudo-charge density along the As–Sb, the Sb–Sb and the Sb–Ga bonds is shown in Fig. 2. Charge is accumulated along the bonds and along the direction to the missing neighbour at the surface, confirming the nearly sp^3 character of the bonding. The bond lengths for the three favourable structures are $d_{Ga-Sb} = 2.55$ (ECLS), 2.61 (p^3), 2.67 Å (EOTS) and $d_{Sb-As} = 2.64$ (ECLS), 2.79 (p^3), 2.77 Å (EOTS). The corresponding values, $d_{Ga-Sb} = 2.81$ (EOCS), 2.76 Å (dimer) and $d_{Sb-As} = 3.14$ (EOCS), 2.96 Å (dimer) are remarkably larger than the sums of covalent radii $d_{Ga-Sb} = 2.66$ Å and $d_{Sb-As} = 2.60$ Å. The shortness of the bond lengths explains the advantages of the ECLS geometry. In the case of the p^3 structure and the EOTS the corresponding bonds are somewhat stretched. We relate the lower adsorption energy of the p^3 structure with respect to the EOTS to the disadvantageous angle between the As dangling orbital and the adatom. The EOTS enables the adatoms to bind both to As and Ga in the underlying substrate layer. Indeed the bond length d_{Sb-As} is 0.2 Å shorter in the EOTS case than we found for the p^3 structure. However we find for the EOTS d_{Ga-Sb} to be 0.06 Å larger since the bonding angle of Sb to the Ga p_z orbital is less ideal. The EOCS and the dimer model completely fail the bond test.

The most important parameters of the atomic geometry of the Sb monolayer and the underlying relaxed GaAs(110) surface are listed in Table 1. The structures according to local minima of the total energy surface show different degrees of agreement with experimental data from Ford et al. [9]. Their LEED analysis considered two structures. The structural parameter predicted for the ECLS are in excellent agreement with our results as can be seen in Table 1. The counter relaxation within the first GaAs layer, $\Delta_{2,\perp}$, as well as the buckling of the Sb–Sb chains, $\Delta_{1,\perp}$, are closer to the LEED values than the corresponding tight-binding results [6]. The LEED data were also interpreted assuming a p^3 structure. They predict an angle between the Sb-chain and the underlying Ga-atom of about 52° whereas we find 77° for the p^3 structure and 80° for the EOTS. There is also an appreciable difference between the tilt angle of the first substrate layer predicted by LEED of $-1.7°$ and the calculated values of $-9.5°$ (p^3) and 1.3° (EOTS). Although the procedure involved in LEED analysis is very complex, we expect that these differences are due to the rather hypothetical character of the p^3 structure and the EOTS. The most pronounced discrimination of the models discussed in Table 1 results from the vertical adsorbate–substrate distance $d_{12,\perp}$. Only the value of the ECLS is in reasonable accordance with the result of X-ray-standing-wave (XSW) studies [17] reporting $d_{12,\perp} = 2.27 \pm 0.05$ Å.

Further indications for the validity of a geometry model follow from a comparison of calculated surface bands and measured band dispersions [18,19]. Such a comparison is presented in Fig. 3 for the highest occupied interface bands. The degree of agreement of the calculated bands with the experimental results is in a wide range

Table 1
Structural parameters in Å for the geometries of the GaAs(110)–Sb (1 ML) system; the present results (obtained for 8/18 Ry cut-off energy) are compared with the results of the LEED analysis by Ford et al. [9], the tight-binding results of LaFemina et al. [6], 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 [9]		0.08				
Tight-binding [6]		0.04		0.33	0.13	
Ab initio [10]		0.04	0.66			
Present results	$\Delta_{1,y}$	2.00/2.00	1.94	2.04	2.28	2.52
LEED [9]		1.99				
Tight-binding [6]		1.86		1.83	2.11	
Ab initio [10]		1.91	1.93			
Present results	$d_{12,\perp}$	2.35/2.36	2.89	2.73	2.43	2.76
LEED [9]		2.34				
Tight-binding [6]		2.35		2.93	2.11	
Ab initio [10]		2.36				
Present results	$d_{12,y}$	4.51/4.50	0.52	1.41	1.41	5.56
Tight-binding [6]		4.47		1.25	1.74	
Present results	$\Delta_{2,\perp}$	0.08/0.10	−0.23	0.03	0.04	0.06
LEED [9]		0.11				
Tight-binding [6]		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 [9]		1.40				
Tight-binding [6]		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
	$d_{23,y}$	2.71/2.70	2.76	2.71	2.80	2.76

of the surface Brillouin zone roughly the same for the ECLS and the EOTS. This holds in particular for the nearly degenerated bands S_3 and S_4 in the stomach gap (pocket) of the projected bulk valence bandstructure. Their dispersion is almost perfectly reproduced. In principle the experimental findings near the top of the valence band can be described by the theory, especially when the adatom-related bands S_5 and S_6 as well as the anion-derived surface state A_2 are taken into account. However, the agreement is not perfect. Probably, the EOTS has to be excluded. This model causes a dispersion of the upper interface bands near $\bar{X}'$ which is too strong. The appearance of the highest occupied state at this critical point contradicts the measured results. We also mention that the EOCS and the dimer model give rise to a metallic surface in contrast to experimental observations. The metallic character of the dimer model may be due to the fact that we found the relaxed Sb atoms nearly equidistant (within 4%) placed, forming a linear chain in [001] direction in this case. The three other structures under consideration turned out to be semiconducting. For the ECLS we find a indirect band gap of about 0.9 eV.

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 ionization energy corresponds to the difference between this potential barrier and the valence band maximum. For the relaxed GaAs(110) surface and the three Sb/GaAs(110)-(1 ML) systems lowest in energy, we get the following results: GaAs(110): 5.5, ECLS: 5.0, EOTS: 4.8 eV, and p^3 structure:

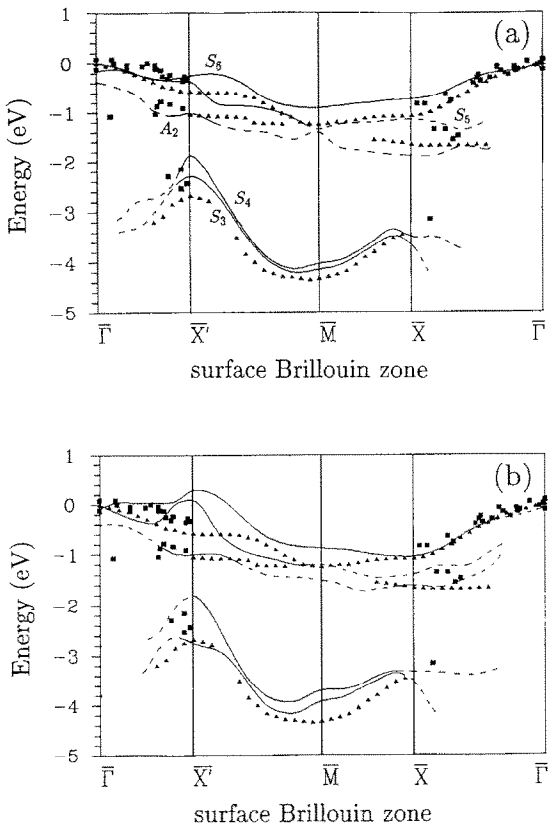

Fig. 3. Comparison of the dispersion of surface bands for Sb/GaAs(110) (1 ML) computed for the ECLS (a) and the EOTS (b) with ARPES values of Ref. [18] (squares) and Ref. [19] (triangles). Solid lines indicate bound states whereas dashed lines denote resonance states. The theoretical and experimental values are aligned at the highest occupied surface state at 0 eV at Γ.

4.4 eV. The difference of the ionization energy of the ECLS and the one calculated for the GaAs(110) surface of about −0.5 eV is closer to the experimental result of −0.3 eV [20] than the numbers calculated for the other structures and provides a further proof that the ECLS is the most likely model.

The examination of structures according to a lower coverage gives insight in the adsorption sites preferred in the initial stage of the interface formation and at the edges of ordered Sb islands with local 1×1 symmetry and allows to estimate the Sb–Sb interaction. We have calculated the total energy for one Sb atom at more than thirty positions within the irreducible part

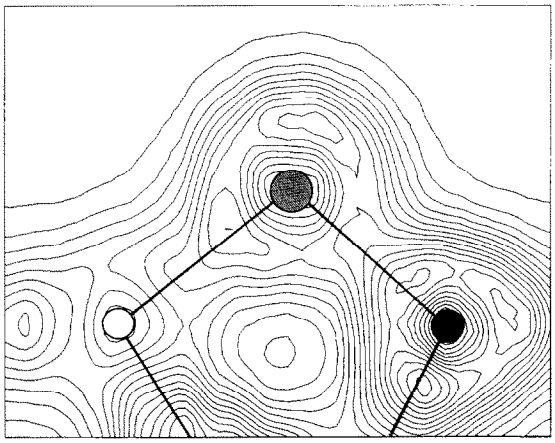

Fig. 4. Contour plots of the valence pseudo-charge density for the $\theta = \frac{1}{2}$ adsorption of Sb on GaAs(110) in the long-bridge bond position. The density is plotted along a plane perpendicular to the surface containing the bonds from the adatom to both As and Ga atoms. The contour step is 0.005 bohr^{-3}.

of the GaAs(110) 1×1 surface unit cell. We find the minimum energy configuration of the Sb in a long-bridge bond position between the As and the Ga atom. The strong covalent bonds of Sb both to As and Ga can be seen in Fig. 4. As one should expect from the electronegativities, the bonding charge is closer to the Sb and As sites, respectively, than to the Ga site. Sb forms an angle of about 101° with As and Ga atoms, thus indicating a mixture of Sb p_σ and sp^3 bonds involved. The bonds are with 2.88 Å (Ga–Sb) and 2.74 Å (As–Sb) somewhat longer than in the ECLS and explain partly that the adsorption energy of 3.89 eV is considerable lower than the value which we found for the ECLS. More important, the coverage $\theta = 1$ also enables a strong Sb–Sb interaction, further increasing the adsorption energy and completely changing the character of the bonding. The total energy surface is characterized by quite rectilinear channels in [$\bar{1}$10] direction. These channels have flat barriers in front of the Ga (0.35 eV) and the As (0.18 eV) dangling bonds and are seperated from each other in [001] direction by about 1.2 eV. That means the Sb atoms can move rather freely on the surface, but the migration should be highly anisotropic. We mention that the STM images [1] in the low-coverage regime seem to indicate

islands with a larger extent in [$\bar{1}$10] direction.

Because of the predicted highly anisotropic mobility of Sb atoms on GaAs(110) also systems with surface unit cells larger than 1×1 structures should be considered. That is why we have additionally studied three 2×1 or 1×2 reconstructed Sb/GaAs(110) surfaces for the half-monolayer case. One of the geometries 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. For this structure we found the adsorption energy with 4.25 eV to be somewhat smaller than in the ECLS case. This reduction is due to the vanishing interaction of second-nearest neighbour Sb atoms in [001] direction and a different relaxation of the substrate. However the missing-chain model gives rise to a about 0.4 eV higher adsorption energy than we found for the long-bridge bond position. Linear and zig-zag chains of Sb atoms grown in [001] direction turn out to be less favourable with 3.46 and 3.83 eV, respectively.

In conclusion, we have studied different structures of the Sb adsorption on the GaAs(110) surface. For a coverage of 1 ML we find both electronic and structural data related to the ECLS in close agreement to experimental results. This structure also gives rise to the highest adsorption energy. We therefore strongly suppose the ECLS to be the actual adsorption structure for 1 ML. The total energy surface for one Sb atom per GaAs pair shows that for very low coverages a long-bridge bond position should occur. For submonolayer coverage we find however also strong interaction between the Sb atoms, accompanied with a high mobility at least in [$\bar{1}$10] direction. Together with the higher adsorption energy realized in the ECLS we expect therefore the Sb atoms to cluster, resulting in islands with local 1×1 symmetry.

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