Geometry and core-level shifts of As on GaAs(110)

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The atomic structure of the As-covered GaAs(110) surface in one-monolayer coverage is studied using the pseudopotential density-functional theory. We compare the adsorption geometry of As/GaAs(110) with that of the well-studied isoelectronic Sb/GaAs(110) system and discuss the large difference in the desorption temperature found in both systems, based on the calculated adsorption energies. In addition, we calculate the As $3d$ and Ga $3d$ core-level shifts at As/GaAs(110) using initial-state theory. Our calculations not only produce well the surface components resolved in a recent photoemission experiment, but predict an additional surface core level for the substrate As atom bonded to the adsorbed As atom. [S0163-1829(99)02219-5]

The interaction of adsorbed group-V elements with the (110) surface of III-V semiconductors is important in connection with the formation of semimetal-semiconductor interface. In particular, the Sb monolayer on the GaAs(110) surface has been extensively studied both experimentally and theoretically because this interface is known to be abrupt and unreactive.[1] As a similar group-V overlayer system, the adsorption of As on the GaAs(110) surface can provide additional information about the chemical reactions between group-V elements and GaAs(110), but this system has been less studied than the Sb/GaAs(110) system.

In a theoretical study of the GaAs(110) surface, Northrup[2] found that in the extreme As-rich limit a 1×1 structure composed of As chains (i.e., the structural model of Fig. 1) is energetically more stable than the Ga-As chain structure produced by cleaving the bulk. Recently, He *et al.*[3] studied the bonding characteristics of As overlayer on GaAs(110) using photoemission experiment. They resolved two surface components from their As $3d$ core-level spectra, indicating two distinct bonding sites of the adsorbed As atoms. This is analogous to the results for the Sb $4d$ core-level shifts at the Sb/GaAs(110) interface, where two well-resolved Sb $4d$ core levels were observed.[4–6] He *et al.*[3] also pointed out that there exists a large difference in the thermal stability of the adsorbed overlayer between As/GaAs(110) and Sb/GaAs(110): While the Sb overlayer is stable up to a substrate temperature of about 550 °C, the As overlayer is removed even by heating above about 100 °C.[3,7,8] Compared to the well-studied Sb/GaAs(110) system, however, As/GaAs(110) still needs more study for a unified understanding of its structure, chemical bonding, and thermal behavior.

In this paper, we have determined the adsorption geometry and energetics of an As monolayer on GaAs(110) using the pseudopotential density-functional total-energy calculation scheme. The calculated geometrical parameters agree well with those of the previous pseudopotential calculation of Northrup.[2] We find that on GaAs(110) the binding of the As overlayer is significantly weaker than that of the Sb overlayer, explaining the large difference in the desorption temperature of the adsorbed overlayer in both systems. We have also calculated the As $3d$ and Ga $3d$ core-level shifts at the As/GaAs(110) surface using initial-state theory. Our results provide an interpretation of the two surface components observed in a recent core-level spectra.[3] Moreover, our theory predicts that the substrate As atom bonded to the adsorbed As atom also produces an additional surface core level. This prediction of three As $3d$ surface core-level shifts reflects well the chemical bonding of As atoms in the As/GaAs(110) interface.

The total-energy calculations are performed using the plane-wave-basis pseudopotential method within the local-density approximation (LDA).[9] We use the Ceperley-Alder[10] exchange-correlation functional for the LDA calculations. The nonlocal ionic pseudopotentials of As and Ga are generated by the scheme of Troullier and Martins[11] in the separable form of Kleinman and Bylander.[12] We simulate the As/GaAs(110) interface by a periodic slab geometry: Each slab contains nine GaAs substrate layers and one 1-ML As overlayer on each side of the slab, and the vacuum region has a thickness of five atomic layers. In the structure optimization, we relax the As and Ga atoms in the top five layers

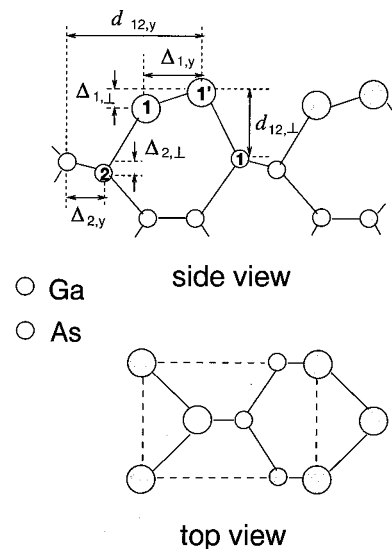

FIG. 1. Schematic diagram of side and top views of the As/GaAs(110)-1x1 surface: the ECLS model.

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TABLE I. Calculated geometrical parameters (see Fig. 1) in Å for the As/GaAs(110) surface in comparison with previous theoretical results. For comparison, the geometrical parameters for Sb/GaAs(110) are also given.

		$\Delta_{1,\perp}$	$\Delta_{1,y}$	$d_{12,\perp}$	$d_{12,y}$	$\Delta_{2,\perp}$	$\Delta_{2,y}$
As/GaAs(110)	Ref. 2	0.01	1.58	2.05	4.36	0.02	1.45
	this study	0.01	1.57	2.06	4.32	0.04	1.48
Sb/GaAs(110)	Ref. 14	0.05	2.00	2.35	4.51	0.08	1.38
	Ref. 13	0.06	1.98	2.38	4.53	0.07	1.45

along the calculated Hellmann-Feynman forces until the remaining forces are all within 6 mRy/Å. We use a plane-wave basis with a kinetic energy cutoff of 10 Ry and a uniform grid of 24 **k** points in the (1×1) surface Brillouin zone. These parameters are found to produce well-converged results for the atomic geometries of both As/GaAs(110) and Sb/GaAs(110).[13]

We consider two structural models for As/GaAs(110): the epitaxial continued layer structure (ECLS) and epitaxial on top structure (EOTS) models, which have been competing as a favorable model for the Sb/GaAs(110) interface.[1,14] In our previous paper of Sb/GaAs(110),[13] the ECLS model was calculated to be more stable than the EOTS model by $\Delta E_{\mathrm{ad}}=0.27$ eV/adatom in adsorption energy. Similarly, the present As/GaAs(110) interface favors the ECLS model by $\Delta E_{\mathrm{ad}}=0.34$ eV/adatom. The geometry of the ECLS model is shown in Fig. 1, and the calculated geometrical parameters are listed in Table I, in comparison with those of an earlier pseudopotential calculation of Northrup.[2] Both the present and previous[2] calculations show the overall good agreement for various geometrical parameters. To our knowledge, there are no experimental data to be compared. The present bond lengths between the surface atoms are $d_{\mathrm{As(1)\text{-}As(1')}}=2.54$ Å, $d_{\mathrm{As(1')\text{-}Ga(1)}}=2.45$ Å, and $d_{\mathrm{As(1)\text{-}As(2)}}=2.46$ Å, where As(1) and As(1′) are the adsorbed atoms and As(2) and Ga(1) are the substrate top-layer atoms. These values are very close to those of the previous calculation[2] ($d_{\mathrm{As(1)\text{-}As(1')}}=2.55$ Å, $d_{\mathrm{As(1')\text{-}Ga(1)}}=2.42$ Å, and $d_{\mathrm{As(1)\text{-}As(2)}}=2.46$ Å). In Table I, we also compare the equilibrium atomic geometry of As/GaAs(110) and Sb/GaAs(110). Our calculated vertical shears of the first- and second-layer atoms in As/GaAs(110) ($\Delta_{1,\perp}=0.01$ Å and $\Delta_{2,\perp}=0.04$ Å) is more reduced than those in Sb/GaAs(110) [$\Delta_{1,\perp}=0.06(0.05)$ Å and $\Delta_{1,\perp}=0.07(0.08)$ Å in Refs. 13 and 14]. We believe that this decrease of the vertical shears in As/GaAs(110) is possibly due to the reduction of the geometrical and electronic inequivalence between the adsorbed overlayer and the substrate compared to the case of Sb/GaAs(110).

Experimentally, it has been known that the adsorbed As atoms in As/GaAs(110) desorb at much lower temperature ($T\approx100\,^\circ$C) compared to the desorption of the Sb atoms in Sb/GaAs(110) ($T\approx550\,^\circ$C).[3,7,8] For an understanding of this large difference in the desorption temperature of the Sb and As overlayers on GaAs(110), we compare the adsorption energies of both systems in Table II. We find that on GaAs(110) the adsorption energy of the As overlayer is much smaller than that of the Sb overlayer by $\Delta E_{\mathrm{ad}}=0.65$ eV/adatom, indicating that the binding of the As overlayer is weaker than that of the Sb overlayer. In order to investigate the different bonding interaction of the adsorbed overlayer between As/GaAs(110) and Sb/GaAs(110), we calculate the formation energy (E_{ch}) of single isolated zigzag chains of As and Sb atoms, where we assume that the bond length and the chain angle have the same values as in the optimized geometry of As/GaAs(110) and Sb/GaAs(110). We find that the formation energy of the isolated As chain is significantly smaller than that of the corresponding Sb one by $\Delta E_{\mathrm{ch}}=0.76$ eV/atom, comparable to the above calculated $\Delta E_{\mathrm{ad}}=0.65$ eV/adatom. Thus, we can say that the large difference of the formation energy between the isolated As and Sb chains is primarily responsible for the different binding of As and Sb atoms on the GaAs(110) substrate. In this sense, the smaller adsorption energy in As/GaAs(110) is attributed to the weaker bonding of p^2-bonded As chain, and therefore As atoms desorb easily at the relatively lower temperature compared to the Sb desorption on GaAs(110).

X-ray photoemission spectroscopy (XPS) studies have provided useful information about the local geometry of V overlayer on GaAs(110) since core-level spectra reflect different chemical environments at the interface.[3–6] Recently, He *et al.*[3] obtained two well-resolved As $3d$ surface components and no Ga $3d$ surface components from the core-level spectra of As/GaAs(110). Using the argument of the different charge accumulation around the adsorbed As atoms, they suggested that the lower (higher) binding energy component is associated with the As atom bonded to the substrate Ga (As) atom since the As-Ga bond has a partly ionic character due to the larger electronegativity of As. This different chemical environment for the adsorbed As atoms is similar to the case of the adsorbed Sb atoms on GaAs(110), where two distinct bonding sites produce two well-resolved Sb $4d$ core-level shifts.[4–6]

In order to identify the origin of the measured core-level shifts at As/GaAs(110), we calculate the As $3d$ and Ga $3d$ core-level shifts using initial-state theory. The initial-state shift is defined by the difference of the eigenvalues of a given core level at different sites. Here, this shift is calculated by evaluating the expectation value of the self-

TABLE II. Comparison of the calculated adsorption energies (E_{ad}) for the As/GaAs(110) and Sb/GaAs(110) surfaces. The formation energies of isolated As and Sb chains (E_{ch}) are also included.

	E_{ad} (eV/atom)	E_{ch} (eV/atom)
As/GaAs(110)	3.90	2.63
Sb/GaAs(110)	4.55 [a]	3.39

[a]Reference 13.

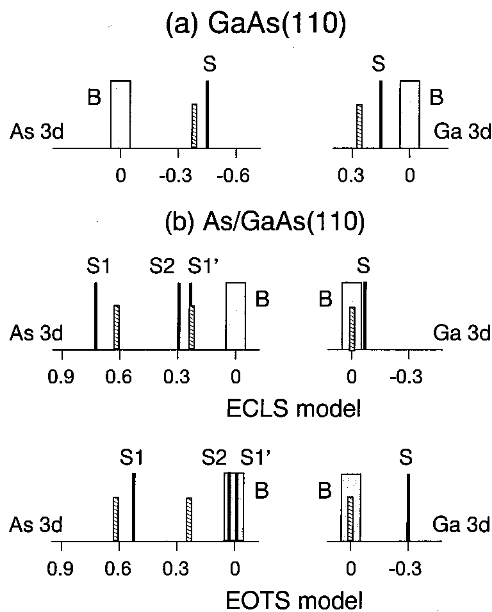

FIG. 2. Calculated As $3d$ and Ga $3d$ surface core-level shifts (solid stick) at (a) the clean GaAs(110) and (b) As/GaAs(110) surfaces in comparison with photoemission experiments (hatched stick). For As/GaAs(110) the results of the ECLS and EOTS models are given. The shifts are given in eV with respect to the bulk value, where the positive (negative) sign indicates a shift to higher (lower) binding energy.

consistent potential on the As $3d$ and Ga $3d$ atomic orbitals, which are computed in the atomic calculation.[13,15,16] This initial-state theory has been successfully applied for III-V semiconductor surfaces.[13,16] In Fig. 2, the calculated surface core-level shifts at As/GaAs(110) are shown in comparison with the calculation for clean GaAs(110) and the XPS data.[3]

Within the ECLS model for As/GaAs(110), we find that the adsorbed As atoms, As(1) and As($1'$), produce two surface core levels $S1$ and $S1'$ with higher binding energy shifts at $+0.73$ and $+0.24$ eV relative to the bulk core level, respectively. The substrate As(2) atom also produces a large surface shift at $+0.29$ eV ($S2$), while the core level (S) for the Ga(1) atom is nearly degenerate with the bulk value. These results for the ECLS model are compared well with the XPS data obtained by He *et al.*[3] (see Fig. 2), where two As $3d$ surface components were resolved at $+0.61$ and $+0.23$ eV and assigned to the two adsorbed As atoms, As(1) and As($1'$), respectively. Our calculations produce quantitatively the binding energies of the observed surface components and also provide an additional information that the substrate As(2) atom contributes to the large surface shift. We find that there is a noticeable difference in the As $3d$ and Ga $3d$ core-level shifts between the ECLS and EOTS models (see Fig. 2). Unlike the ECLS model, the EOTS model produces only one As $3d$ surface core-level shift at $+0.53$ eV, which originates from the adsorbed As atom bonded to substrate As atom, and instead its substrate Ga atom produces a lower binding surface shift at -0.30 eV. These core-level shifts of the EOTS model disagree with the experimental observations.[3]

Finally, we compare the As $3d$ and Ga $3d$ core-level shifts between the As/GaAs(110) and clean GaAs(110) surfaces. In the clean GaAs(110) surface, we find two surface core-level shifts for the top-layer As and Ga atoms: As (Ga) $3d$ core level shifts to lower (higher) binding energy by 0.45 (0.15) eV, in good agreement with experimental values of 0.37 (0.28) eV.[17] These surface core levels undergo significant changes by the adsorption of As atoms in As/GaAs(110); that is, the As $3d$ surface core level located at -0.45 eV moves to the higher binding energy side [i.e., to the level $S2$ in Fig. 2(b)], and the Ga $3d$ surface core level at $+0.15$ eV moves to the near bulk value (S). These changes can be explained by the fact that the Ga(1) atom in As/GaAs(110) recovers a near-bulk-like environment by the formation of tetrahedral bonds with four As atoms, while the As(2) atom is still in a different chemical environment from the bulk As atom. As(2) is bonded to one adsorbed As atom and three Ga atoms, unlike the bulk As atom bonding tetrahedrally with four Ga atoms. Based on a simple argument of charge transfer on the partly ionic As-Ga bond, $S2$ for As(2) is expected to shift to a higher binding energy relative to the bulk value.

In summary, we determined the atomic geometry and core-level shifts of the 1-ML As-covered GaAs(110) surface using the pseudopotential density-functional theory. The present results for the geometrical parameters agree well with previous pseudopotential calculation. From the calculations of the adsorption energy of As and Sb overlayers on GaAs(110) and the formation energy of isolated As and Sb chains, we found that the easy desorption of the As overlayer is attributed to the weaker As-As bonding in the As chain. Our results for the As $3d$ and Ga $3d$ core-level shifts confirm the assignment of the atomic origin for the surface components observed in recent photoemission core-level spectra and also predict an additional surface core level for the substrate As atom bonded to the adsorbed As atom. The calculated core-level shifts are well correlated with the chemical bonding of As and Ga atoms in the As/GaAs(110) interface.

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