Sb Overlayers on (110) Surfaces of III-V Semiconductors: Structure and Bonding

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The atomic geometry, chemical bonding, and surface-state eigenvalue spectra are predicted for saturated (1×1) ordered monolayers of Sb on the (110) surfaces of GaP, GaAs, GaSb, InP, InAs, and InSb. For GaAs and InP the predicted geometries are in good correspondence with those obtained from low-energy electron diffraction. The predicted electronic structure of these Sb-substrate systems reveals a novel type of bonding not found in either bulk III-V semiconductors or molecular III-V analogs.

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The prediction of the atomic geometries of overlayers on compound semiconductors is a topic of considerable current interest, especially with regard to the mechanisms of Schottky-barrier formation and the growth (e.g., by molecular beam epitaxy) of multilayer heterojunction systems.[1] Moreover, such geometries are now being determined experimentally, for example by elastic low-energy electron diffraction (ELEED) intensity analyses.[2,3] Thus, an opportunity exists to develop and test predictive models of the geometrical and electronic structure of ordered overlayers on semiconductor surfaces. Our purpose herein is to present an extension to such systems of our tight-binding model utilized for the prediction of the atomic geometries and surface-state eigenvalue spectra of the clean (110) surfaces of III-V semiconductors: a model which is known to predict accurately the measured geometries of these surfaces.[4]

The particular systems which we examine are ordered (1×1) monolayers of Sb on the (110) surfaces of GaP, GaAs, GaSb, InP, InAs, and InSb. The absorption of Sb on GaAs(110) and InP(110) has been the subject of numerous recent experimental photoemission studies.[5-10] Moreover, an ELEED structure analysis of GaAs(110)-$p(1\times1)$-Sb(1 ML) (ML denotes monolayer) has been reported[11] and utilized as the basis for a calculation of the surface-state eigenvalue spectrum.[12] Hence Sb on GaAs(110) affords an ideal test for our unified model of *both* the surface atomic geometry *and* the surface-state eigenvalue spectrum because it is the only semiconductor-overlayer system for which both quantities have been determined independently. Moreover, the detailed nature of the bonding of the Sb monolayer to the GaAs(110) substrate has remained an enigma because the experimental geometry, shown in Fig. 1, is incompatible with simple models of p^2 and sp^3 bonding.[11]

We determine the atomic geometries via a total-energy minimization method[13] and calculate the associated surface-state eigenvalue spectra using scattering theory.[14-16] Both the total-energy minimization and the calculation of the surface-state eigenvalue spectrum were performed using the

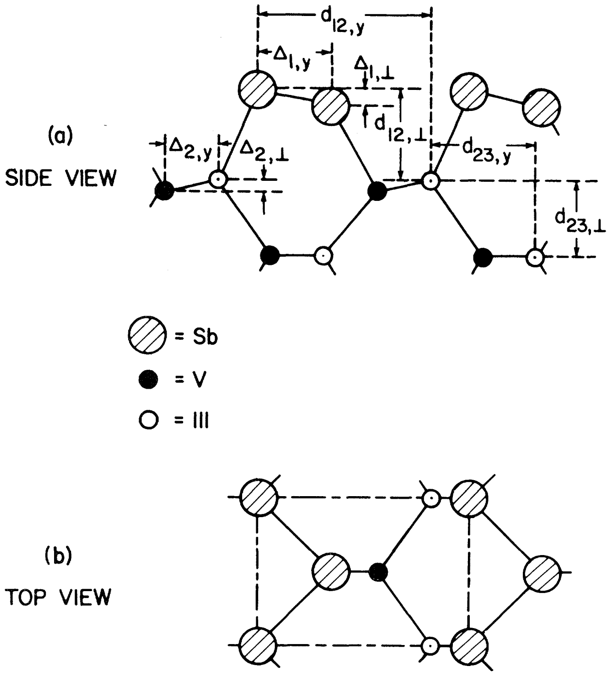

FIG. 1. Schematic diagram of the surface geometry for III-V(110)-$p(1\times1)$-Sb(1 ML) and definition of the structural parameters. Panel (a): Side view. Panel (b): Top view.

TABLE I. Structural parameters predicted for the atomic geometries of III-V(110)-$p(1\times1)$-Sb(1 ML) systems defined in Fig. 1. The values enclosed in parentheses were determined via ELEED for GaAs(110)-$p(1\times1)$-Sb(1 ML) (Ref. 11) and for InP(110)-$p(1\times1)$-Sb(1 ML) (Ref. 18). Units are angstroms, and a_0 is the bulk lattice constant of the substrate.

System	a_0	$\Delta_{1,\perp}$	$\Delta_{1,y}$	$d_{12,\perp}$	$d_{12,y}$	$\Delta_{2,\perp}$	$\Delta_{2,y}$
GaP	5.451	0.34	1.89	2.12	3.91	0.00	1.36
GaAs	5.654	0.09	1.87	2.29	4.39	0.08	1.42
		(0.10 ±0.05)	(1.96 ±0.3)	(2.39 ±0.1)	(4.62 ±0.3)	(0.10 ±0.05)	(1.41 ±0.3)
GaSb	6.118	0.07	1.80	2.25	4.73	0.18	1.57
InP	5.869	0.57	2.02	2.23	4.00	0.09	1.47
		(0.70 ±0.1)	(1.98 ±0.3)	(2.43 ±0.1)	(4.46 ±0.3)	(0.00 ±0.1)	(1.47 ±0.3)
InAs	6.036	0.22	1.76	2.23	4.34	0.20	1.54
InSb	6.478	0.13	1.68	2.21	4.74	0.20	1.68

nearest-neighor sp^3s^* empirical tight-binding model of Vogl, Hjalmarson, and Dow.[17] A detailed description of the model is given elsewhere.[4] In Table I we give the structural parameters, defined in Fig. 1, that characterize the minimum-energy atomic structure of ordered Sb monolayers on GaP, GaAs, GaSb, InP, InAs, and InSb. The shear vector between the two Sb atoms perpendicular to the (110) surface, $\vec{\Delta}_1$, is compared with the value determined by ELEED for GaAs (Ref. 11) and the results of a preliminary ELEED analysis[18] for InP. As seen from this comparison, these predictions of $\vec{\Delta}_1$ are in quantitative agreement with the results of these analyses.

The electronic structure of the minimum-energy $p(1\times1)$ Sb chains on the III-V (110) surfaces is derived via three steps, the results of which are depicted in Fig. 2. First, the eigenvalue spectrum of an isolated (p^2-bonding) Sb chain is presented in panel (a) of Fig. 2. Second, the effect on this spectrum of bonding the chain to a homopolar semiconductor, i.e., unreconstructed Ge(110), is shown in panel (b). The further consequences of the polarity of the III-V substrate are illustrated for GaAs(110) in panel (c).

Three types of states occur for the isolated p^2-bonding Sb chain. The *nonbonding* (*s*-orbital derived) *states* (S_1 and S_2 in Fig. 2) do not contribute to the Sb-substrate bonding. They are little affected by the substrate although the substrate polarity does split their degeneracy along the $\bar{X}$-$\bar{M}$ line as seen in panel (c) of Fig. 2 for Sb on GaAs(110). The *intrachain bonding p states* (S_3 and S_4 in Fig. 2) also are not seriously affected by bonding to the substrate except for the $\bar{X}$-$\bar{M}$ splitting of their degeneracy for polar materials, as shown in panel (c). As $\vec{k}_\parallel$ is varied from $\bar{\Gamma}$ to $\bar{X}$, i.e., along the chain direction, the occupied intrachain p_x^- and p_y^- states mix together in such a way as to preserve bonding character with high electronic density between the Sb atoms. Unoccupied antibonding intrachain states (p_x^+ and p_y^+) lie higher in energy and are not shown in Fig. 2. The bonding *p* states are responsible for the Sb-Sb bonds within the individual p^2-bonded Sb chains. The bonding of these chains to the substrate is generated by the mixing of the π states of the isolated chain (states p_z^+ and p_z^- in Fig. 2) with the dangling-bond orbitals of the nearly unreconstructed substrate to form two occupied *bonding surface state bands* (states S_5 and S_6 in Fig. 2) and two unoccupied *antibonding surface state bands* (states S_7 and S_8 in Fig. 2). The resulting Sb-substrate bonds may be regarded as comprised of bonding combinations of sp^3 hybrid orbitals from the substrate and π-electron orbitals from the Sb chain. Thus, they are *not* conventional sp^3 bonds, although the minimum-energy structure is characterized by nearly sp^3 bond lengths and angles to the substrate. Such hybrid bonds are not characteristic of either bulk III-V compounds or their small molecule analogs. Hence, they seem to exemplify a unique type of surface bonding characteristic of the III-V(110)-$p(1\times1)$-Sb(1 ML) systems. The occurrence of such surface bonds resolves the puzzle noted in the ELEED structure analysis[11] of Sb on GaAs(110) concerning simultaneous occurrence of the p^2 bonding in the SB chain together with sp^3 bond angles of this chain relative to the GaAs substrate. Our calculated surface-state eigenvalues for GaAs(110)-$p(1\times1)$-Sb(1 ML) are similar to

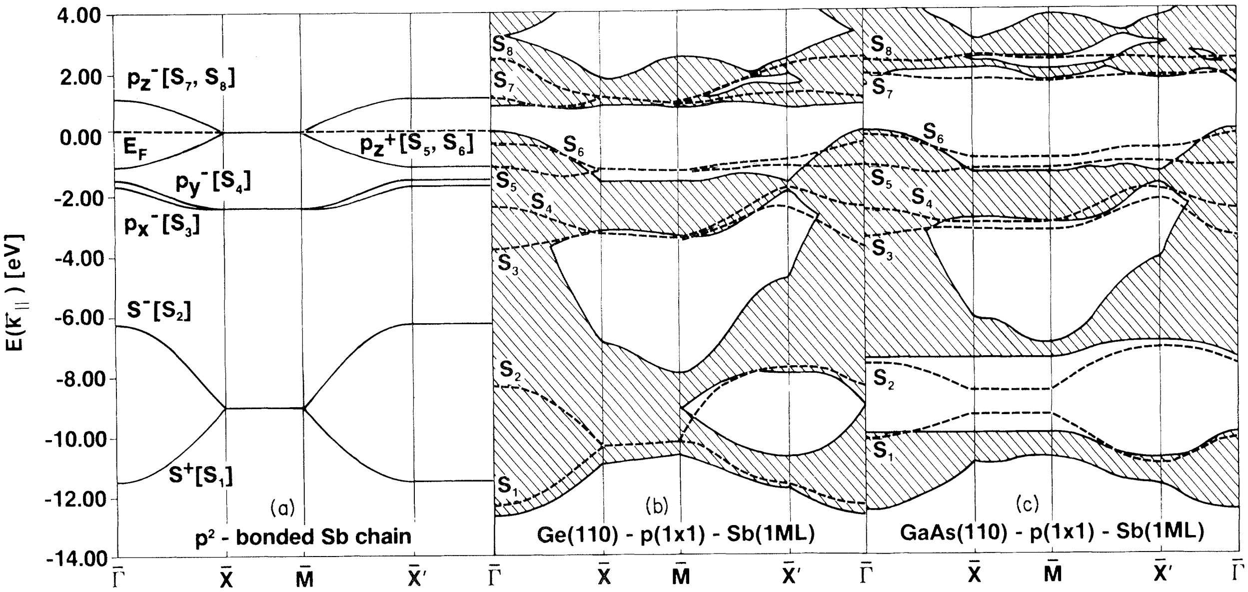

FIG. 2. Panel (a): Energy dispersion for a single (metallic) isolated Sb chain mapped onto the (110) surface Brillouin zone. Panel (b): Energy dispersion of surface bound states and resonances for Ge(110)-$p(1\times1)$-Sb(1 ML). Panel (c): Same as panel (b) for GaAs(110)-$p(1\times1)$-Sb(1 ML). Only Sb-derived surface states are shown.

those of Bertoni *et al.*[12] although the detailed interpretation given above differs significantly from theirs. They are also in agreement with the qualitative results of Skeath *et al.*[8] obtained using a simplified tight-binding Hamiltonian.

In summary, we have predicted the atomic and electronic structure of ordered Sb overlayers on the (110) surfaces of GaP, GaAs, GaSb, InP, InAs, and InSb. The atomic structures determined via total-energy minimization procedures are in quantitative agreement with those obtained from ELEED data analyses for GaAs(110)-$p(1\times1)$-Sb(1 ML) and InP(110)-$p(1\times1)$-Sb(1 ML). Moreover, our analysis reveals a novel type of hybrid Sb-substrate bonding which resolves a puzzle identified in the ELEED structure analysis of GaAs(110)-$p(1\times1)$-Sb(1 ML).

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