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Electron states of an Sb-ordered overlayer on GaAs(110)

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The electronic properties of an Sb overlayer deposited onto a GaAs(110) surface have been calculated using a self-consistent-pseudopotential approach and assuming the ordered-overlayer geometry proposed in recent low-energy electron diffraction studies. The results show that Sb adatoms are bound by strong covalent bonds to the substrate and that various overlayer or chemisorption-induced states appear throughout the valence band. Comparison with photoemission data allows us to assign a major Sb-induced structure appearing in the energy distribution curves.

I. INTRODUCTION

Adsorption of group-III and -V elements on the GaAs cleavage surface has been investigated both theoretically and experimentally in the last few years.[1-10] In many of these systems, as, for example, Al on GaAs(110), experimental studies have shown that the interface structure depends upon the thermal treatment.[1-3] Except for extremely low coverages, where Al atoms are likely to form directional bonds with the substrate,[4] room-temperature deposition for monolayer coverages seems to give rise to disordered overlayers formed by adatom clusters[5] which are weakly bound to the substrate and leave the relaxation of the free surface almost unperturbed. Under such conditions the basic electronic features found in the experimental spectra closely resemble those of the clean surface. After annealing, an intermixed phase is formed through the occurrence of exchange reactions between overlayer and substrate atoms.[1-3,6]

For group-V overlayers evaporated at room temperature onto GaAs(110), angle-resolved ultraviolet photoemission spectra[7] did not report the removal of any surface-sensitive feature and showed only minor adsorbate-induced structures in the energy distribution curves. Similar conclusions were drawn on the basis of electron-energy-loss spectra.[7] Structural analyses by low-energy electron diffraction (LEED) on As deposited onto GaAs(110) (Ref. 8) have shown some ordering of the adatoms in a (1×1) overlayer, although the adsorption is accompanied by a strong increase in the background. No evidence of such ordering has been found for the lighter group-V elements.[9] Such behavior seems to indicate the tendency of group-V atoms to remain in their molecular form rather than to produce ordered overlayers bound to the substrate through strong directional covalent bonds.

A noticeable exception is the deposition of Sb on GaAs(110). Unlike the other group-V elements, room-temperature Sb deposition produces a well-ordered overlayer for a coverage of one monolayer and an abrupt interface.[10-12] Recent photoemission[10] and thermal desorption experiments[12] indicate that the overlayer is strongly bound to the substrate and that it has electronic properties considerably different from those of the clean substrate surface.

We have therefore undertaken a theoretical investigation of the electronic properties of this system with the purpose of clarifying the basic aspects of the chemical bond between the overlayer and the substrate and to provide an explanation of the occurence of chemisorption-induced states in the experimental photoemission spectra. To this end we have applied the self-consistent pseudopotential approach to the calculation of the electronic structure of a slab of GaAs atomic planes with an ordered Sb overlayer on both sides, assuming the overlayer geometry which optimizes the agreement between LEED intensity profiles and dynamical analysis.[11] Our results provide the first theoretical description of this system and allow interpretation of the experimental findings.

II. CHEMISORPTION GEOMETRY

The atomic arrangement of the deposited monolayer of Sb on GaAs(110) has been accurately investigated in a recent study performed by Duke *et al.* by means of a dynamical analysis of LEED intensities.[11] This study shows that the deposition of Sb onto GaAs(110) at room temperature produces a stable and ordered structure, retaining the two-dimensional surface periodicity of the substrate with two Sb atoms per planar unit cell. The interface is sharp and no overlayer-substrate interdiffusion takes place.

For the interpretation of LEED data, different models of $p(1\times1)$ Sb overlayers have been considered, corresponding to different hypotheses about the chemical bond and to various possible geometrical arrangements. The model which leads to the more satisfactory description of the data is represented in Fig. 1 and consists of an ordered overlayer of Sb atoms saturating the dangling bonds of both Ga and As atoms. The saturation of the broken bonds is expected to change the electronic configuration of the outer plane of the substrate and to remove the relaxation of the clean surface, leading to a configuration of the outer GaAs plane closer to an ideal (110) surface. The larger size of Sb relative to Ga and As is accommodated by expanding the Sb-Sb lateral spacing along the y axis (see Fig. 1), leading to a bond angle between the Sb atoms in the chain of nearly 91° and to Ga-Sb and As-Sb distances equal to 2.61 and 2.70 Å, respectively. In this way the atom bound to Ga is located slightly outwards with respect to the one bound to As. The distance between Sb adatoms in the overlayer in 2.8 Å and is close to the Sb bulk nearest-neighbor distance. The first substrate layer presents a slight counter-relaxation (As moves inwards with respect to Ga by 0.1 Å) in complete analogy with the second layer of a free GaAs cleaved crystal.[13]

III. THEORETICAL FRAMEWORK

The method we adopted has already been described in previous papers,[14,15] and here we shall recall only its main features. The first point is to reintroduce the three-dimensional periodicity of the lattice—which is lost with the truncation of the infinite crystal—so that the surface problem can be described with the same formalism of bulk calculations. This is achieved by building up a structure made of slabs of solid, chemisorbed layers, and vacuum, which follow one another along the direction normal to the surface (z axis). In our case each slab is composed by nine regularly stacked GaAs layers with a (110) surface and an Sb overlayer on each side, and it is separated from the contiguous slab by four layers of vacuum. This choice proves to be appropriate to avoid interactions between the two surfaces both through the slab and the vacuum; in fact, surface states resulting from the calculation always appear in nearly degenerate couples. The slab unit cell is then orthorhombic, with a volume 15 times larger than the bulk unit cell. The odd number of planes preserves the $z \rightarrow -z$ symmetry with respect to the central plane of the slab. This symmetry, together with the planar $x \rightarrow -x$ one, is fully exploited choosing symmetry adapted combinations of plane waves as basis functions and solving the secular problem at the high symmetry points of the two-dimensional Brillouin zone (2DBZ). We considered up to 350 plane waves (corresponding to a cutoff of 2.7 Ry); 1100 more plane waves (corresponding to a cutoff of 7.0 Ry) were included via

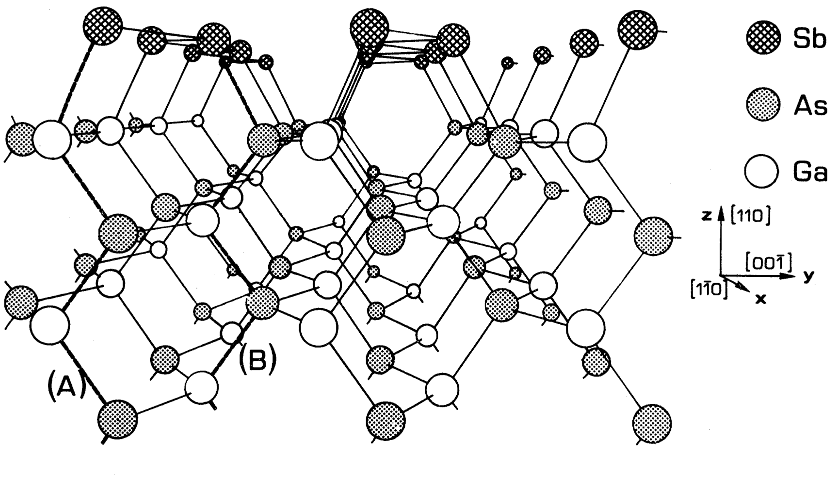

FIG. 1. Side view of four GaAs(110) planes with one Sb overlayer. Chains of atoms along $(1\bar{1}0)$ planes passing either through Ga (chain A) or through As (chain B) surface atoms are indicated.

the Löwdin perturbation technique.[16]

The geometry of the system is directly taken into account in the Hamiltonian through the structure factor

$$S_i(\vec{G})=\sum_{\vec{R}_j^i} e^{-i\vec{G}\cdot\vec{R}_j^i}\,,$$

which enters the definition of the bare pseudopotential

$$V_b(\vec{r})=\sum_{\vec{G}}\sum_i V_i(\vec{G})S_i(\vec{G})e^{i\vec{G}\cdot\vec{r}}\,.$$

Here j runs over all the lattice sites of the ith atomic species in the unit cell and $V_i(\vec{G})$ is the Fourier transform of the bare ionic local pseudopotential. In the present calculation the bare ionic potentials of the substrate have been chosen according to Ref. 17, while for antimony we used the pseudopotential given by Frensley and Kroemer.[18]

The total screened pseudopotential is obtained by adding to the bare pseudopotential the Hartree term $V_H(\vec{r})$ and the exchange-correlation contribution $V_{\text{xc}}(\vec{r})$. This last term has been evaluated as a local functional of the valence pseudocharge-density $\rho_{\text{val}}(\vec{r})$:

$$V_{\text{xc}}(\vec{r})=-\alpha\frac{3e^2}{2\pi}[3\pi\rho_{\text{val}}(\vec{r})]^{1/3}\,.$$

The value of the parameter α has been chosen here equal to 1. Both this choice and the validity of the local-density approximation have been discussed elsewhere.[15]

The total screened pseudopotential and valence charge density are made mutually consistent using an iterative procedure, where starting from a reasonable total potential, a valence charge density is obtained, from which a new total potential is calculated, and so on, until the calculated valence charge density provides a total potential equal to the one that produced it. The convergence of this procedure is optimized according to the method extensively discussed in a previous paper.[19]

IV. PRESENTATION OF THE RESULTS

Before detailing the chemisorption-induced features found in the theoretical results, it is convenient to give a general description of the valence charge distribution. To this end we display in Figs. 2(a) and 2(b) the map of the total valence charge density along $(1\bar{1}0)$ planes perpendicular to the surface and passing through the Sb atoms deposited on surfaces As and Ga, respectively.

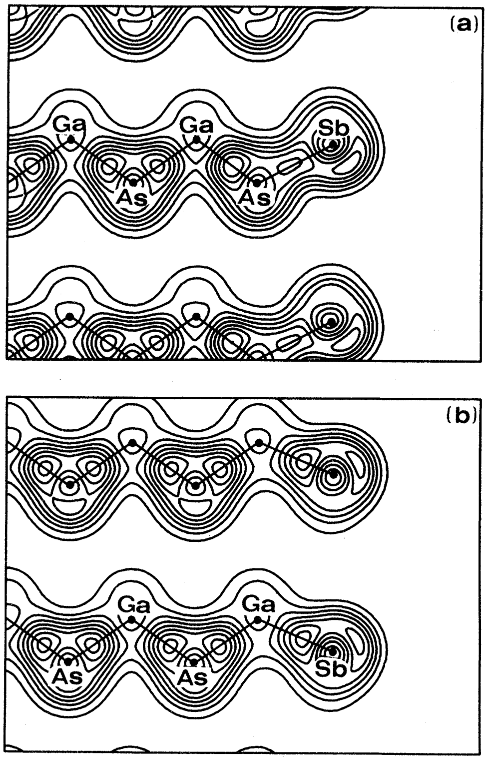

FIG. 2. Contour plots of the total valence pseudocharge-density for Sb deposited on GaAs(110), drawn along $(1\bar{1}0)$ planes passing through (a) As and (b) Ga surface atoms. The contours are spaced by 3.0 electrons per bulk unit cell.

It is clear from these plots that the overlayer atoms are linked to the substrate by directional covalent bonds, similar to those that connect Ga and As atoms with their neighbor in the bulk. This is simply a consequence of the fact that to a large extent our model retains the features of sp^3 hybridization, characteristic of the atoms in the tetrahedral environment. In both Figs. 2(a) and 2(b), Sb charge is accumulated along the direction of the neighbor substrate atoms, as well as in the direction of the missing neighbor at the surface. Although the Sb atoms do not occupy the same sites of Ga and As atoms at the unrelaxed surface, these features are essentially the same found for the free surface and correspond to back and dangling bonds, respectively. Note that since Sb has five electrons in the outer shell, its dangling orbitals are occupied, unlike the clean surface where the Ga dangling-bond state is empty. Such a picture agrees with the main conclusions of the work of Duke *et al.*[10]

There are, however, significant differences between the valence charge distribution for Sb deposited on As and Sb deposited on Ga. In Fig. 2(a) the piling of charge along the back-bond direction appears approximately halfway between the two atoms, indicating a purely covalent bond between Sb and As. In Fig. 2(b) the bonding charge is closer to the Sb site and distributed in the same way as in the Ga—As bond of the bulk crystal. From this respect the deposition of the Sb atoms appears to introduce a more significant perturbation of the bonding charge at the As sites than at the Ga sites.

The bonding between adatoms is illustrated in Fig. 3(a), giving contour plots of the total valence charge density along the overlayer. For comparison we show in Fig. 3(b) the charge density on the first GaAs plane. It is seen that Sb atoms are linked to each other through covalent bonds whose strength is comparable with that of the bonding with the substrate. The differences between the behavior of the charge along Sb chains and that of the substrate are partly due to the ionicity of the bond between Ga and As and partly to the hybridization of the Sb *p* orbitals in the plane with those normal to the surface, which is not the same as in the free GaAs surface.

The surface and chemisorption-induced states at the high-symmetry points of the 2DBZ are plotted in Fig. 4 over the projected bulk band structure of GaAs. Antimony-induced states are indicated by S_i, while A_i and C_i label anion and cation surface states of the substrate. Such notation has been used in previous papers,[15,20] and it is particularly useful

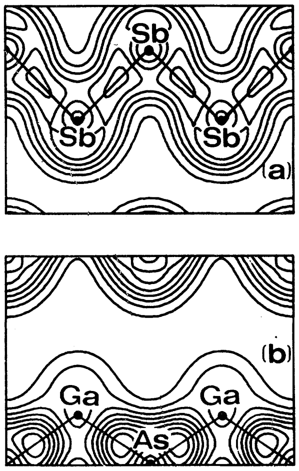

FIG. 3. Total valence pseudo-charge-density plotted along an *x*-*y* plane at the overlayer (a). The projections of the Sb atomic positions are also shown; they are located 0.29 and 0.38 Å out of it. (b) shows the total valence pseudo-charge-density at an *x*-*y* plane containing substrate atoms; due to counter relaxation the As atoms are 0.1 Å below it.

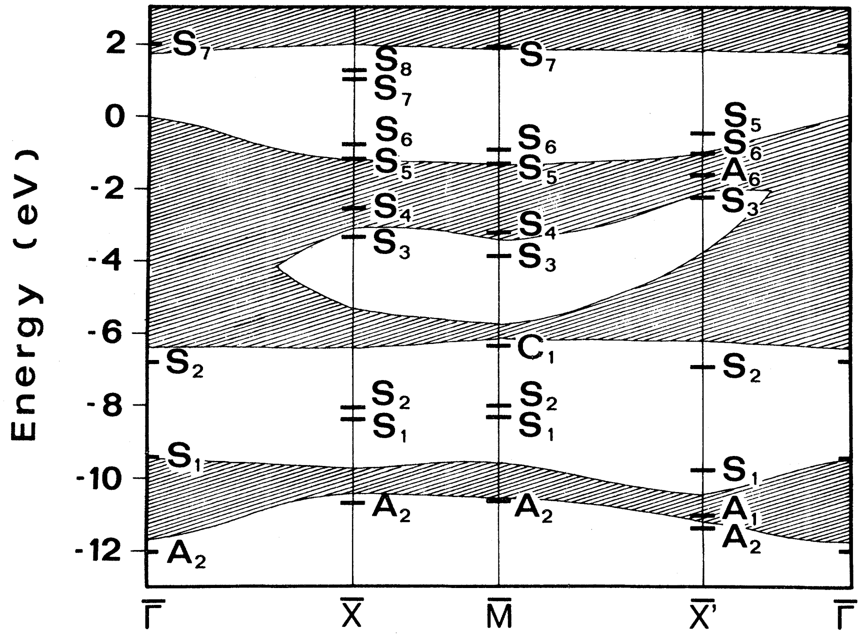

FIG. 4. Projected bulk band structure of the substrate (shaded region) and localized states energies at the high-symmetry points of the two-dimensional Brillouin zone for Sb deposited on GaAs(110). Sb-induced states are labeled by S_i, while A_i and C_i denote anion- and cation-derived surface states, respectively. Energies are referred to the valence-band maximum.

to compare the results for the clean and the chemisorbed surfaces.

In analyzing these features of the electronic spectrum we can distinguish three different classes of states.

(a) Overlayer states correspond to electronic states localized on the overlayer plane and are not directly involved in the bonding with the substrate.

(b) Chemisorption-induced states arise essentially from the coupling between the adatom orbitals and the unsaturated bonds of the substrate. They usually display a pronounced maximum of the valence charge density along the direction of the substrate atoms neighboring the adatoms.

(c) Substrate states are localized in the first plane of the substrate; they usually are surface states of the free surface, slightly modified or shifted in energy by the chemisorption, that do not take part in the chemisorbitive bond. Features of this sort can also be induced by the chemisorption, as a consequence of the modifications of the substrate potential in the external layers.

The orbital character and the space localization of the various states indicated in Fig. 4 can be better illustrated by plotting the charge density along $(1\bar{1}0)$ planes perpendicular to the surface and passing either through the As or the Ga surface atoms.

Figures 5(a) and 5(b) show the charge-density plot for S_1 and S_2 states located in the ionic gap. They are s-like Sb states corresponding to the adatom deposited on As or Ga, respectively, almost completely localized on the overlayer plane. The two bands are flat and nearly degenerate at $\bar{X}$ and $\bar{M}$, where they correspond to states localized on different adatom sites. In fact, the mirror-plane symmetry at these points separates states localized along type-A chains (terminating with Ga—Sb bonds at the surface) and states localized along type-B chains (terminating with As—Sb bonds at the surface). The dispersion increases when going toward $\bar{\Gamma}$ and $\bar{X}'$, where coupling between the two states occurs, since mirror-plane symmetry does not separate states localized along different chains. These two states are not significantly involved in the bond and we can classify them as overlayer states.

The states labeled S_5 and S_6 belong the the same class. As shown by Figs. 6(a) and 6(b), they have the character of dangling Sb orbitals, with maxima of charge pointing out of the surfaces, for adatoms deposited on Ga and As, respectively. Their shape and orientation are rather similar to those of the free-surface dangling bonds. Note that there is almost no contribution to these states from the internal planes, so that they can be properly classified as overlayer states. They retain this character along the high-symmetry lines except near $\bar{\Gamma}$, where they couple with bulk states of the same symmetry. State S_6 has a resonant character also near $\bar{M}$, although it shows a strong maximum at the surface. From the chemical point of view this couple of bands can be identified as due to lone pairs of the Sb atoms, since they accomodate two p electrons not taking part in the bond.

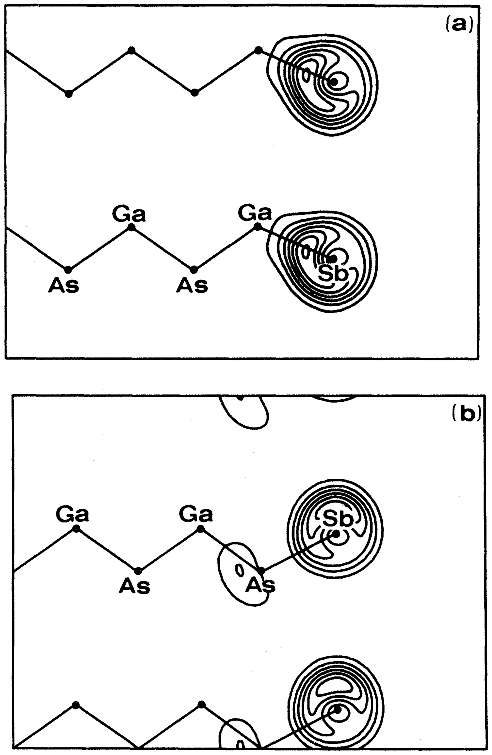

FIG. 5. Charge-density plots for states (a) S_1 and (b) S_2 at point $\bar{M}$. Contours are spaced 0.3 electrons per bulk unit cell.

Two more filled Sb states are found in the upper region of the valence band, denoted by S_4 and S_3 in Fig. 4. They belong to class b, being respectively, bonding combinations of Sb states with the As and Ga sp^3 dangling orbitals of the ideal surface. An inspection of the corresponding charge-density maps [Figs. 7(a) and 7(b)] shows that the charge density is accumulated along the bond direction. S_3 is accomodated along the upper edge of the large lens of the projected bulk band structure in the $\bar{X}$-$\bar{M}$ and $\bar{X}'$-$\bar{M}$ directions. It always has a strong surface character except near the Brillouin zone center. S_4

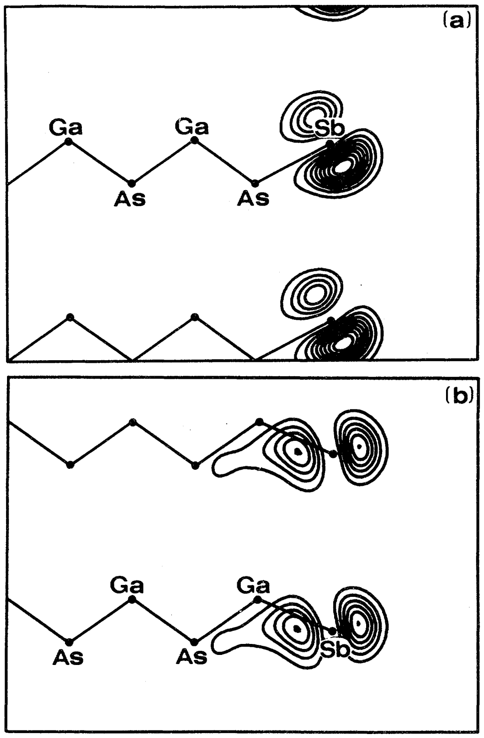

FIG. 6. Charge density distribution of Sb-induced states (a) S_5 and (b) S_6 at $\bar{X}'$, plotted along chains A and B, respectively.

is well defined along the $\bar{M}$-$\bar{X}$ direction, but it becomes a very weak resonance when going toward $\bar{X}'$ and $\bar{\Gamma}$. The corresponding antibonding states are the features labeled S_7 and S_8, respectively, due to Sb-As and Sb-Ga coupling. They have a large contribution from Sb p empty states [see Figs. 8(a) and 8(b)]. S_7 is particularly interesting since it partially overlaps the band-gap region, having a minimum at $\bar{M}$ nearly 0.2 eV below the conduction-band minimum. S_8 has essentially a resonant character and does not show significant charge localization except at $\bar{X}$.

We turn now to discuss the other electronic states which belong to class c. The lowest in energy is state A_2 lying in the region between -12 and -10.5 eV below the valence-band maximum and well defined throughout the two-dimensional Brillouin zone. From the analysis of the map of Fig. 9 it appears to be an s-like As state localized on the first substrate atomic plane. This same feature is found in calculations of the electronic structure of the free surface in both ideal and relaxed configurations,[15,20] but at higher energies, usually near the lower edge of the ionic gap. As a consequence of the slight change in hybridization caused by the Sb

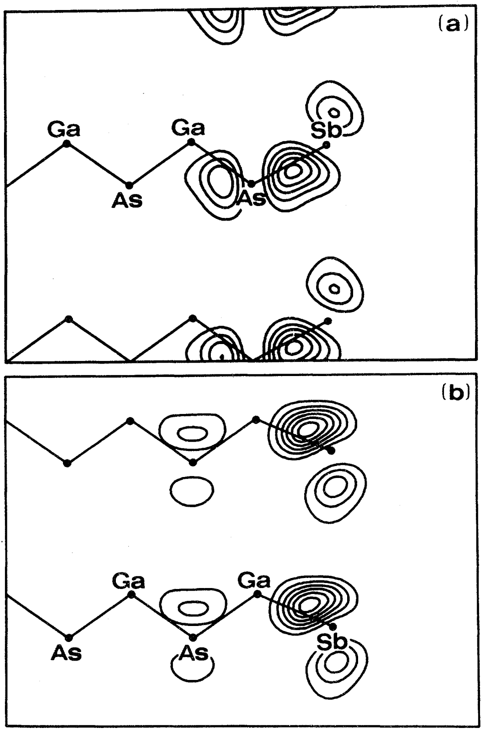

FIG. 7. Charge-density maps for states (a) S_3 and (b) S_4 at points $\bar{M}$ and $\bar{X}$, respectively.

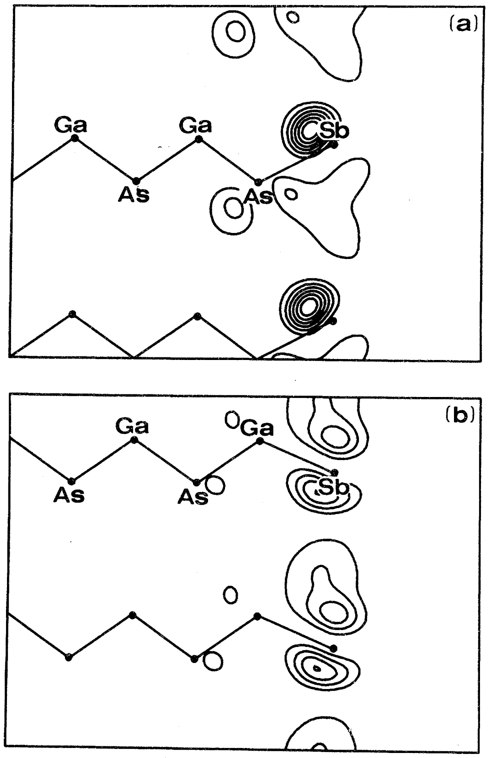

FIG. 8. Charge-density plots for empty antimony-induced states (a) S_7 and (b) S_8 at point $\bar{X}$.

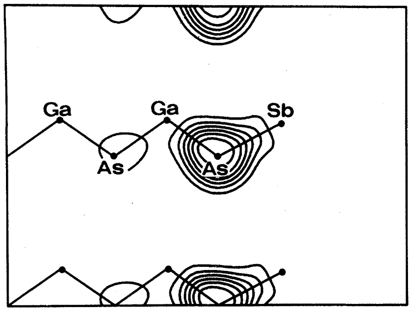

FIG. 9. Surface state A_2; charge-density distribution plot at $\bar{M}$.

depositions, it moves toward higher binding energies while retaining essentially the same orbital composition and shape. The features labeled A_1 and C_1 [Figs. 10(a) and 10(b)] are s states coming from As and Ga atoms of the second substrate layer. Such states do not exist in the spectrum of the ideal GaAs surface, although they can be well identified in the relaxed surface spectrum. They can be interpreted as strong resonances caused by the modification of the potential at the surface induced by the overlayer. State A_6 found at $\bar{X}'$ is a planar surface state which is present in the electronic spectrum of the free surface at nearly the same energy. A plot of its charge density along x-z plane is shown in Fig. 11.

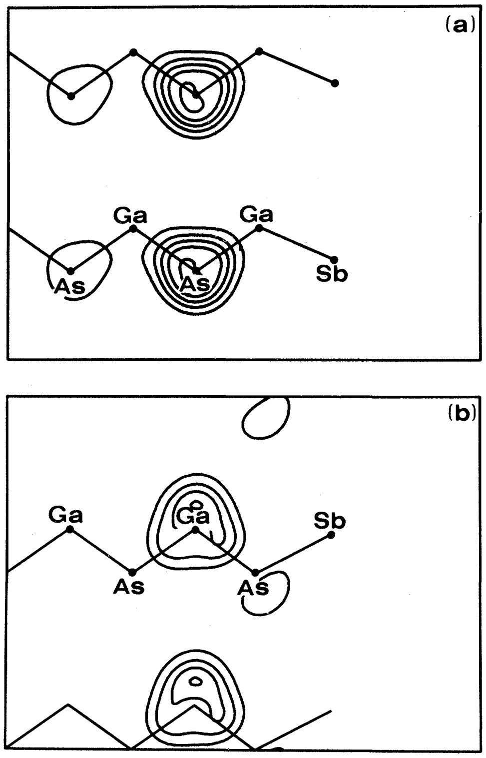

FIG. 10. Surface states (a) A_1 and (b) C_1 charge-density maps at point $\bar{M}$.

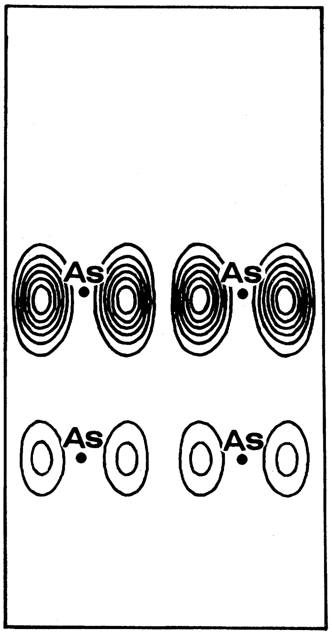

FIG. 11. Charge-density distribution plots for planar surface state A_6 at point $\bar{X}'$, plotted along the x-y plane passing through As surface atoms.

V. INTERPRETATION OF THE EXPERIMENTAL DATA

We can compare the previous theoretical results with the ultraviolet photoemission spectra of Skeath *et al.*[9] These authors found that at coverages of approximately one monolayer a new peak appears at about 1.5 eV below the valence-band maximum. Such a feature is seen at all the photon energies in the range $h\nu = 18-30$ eV. At the same time, the GaAs peak at -2 eV disappears, indicating that a deep rearrangement in the electronic structure takes place at about one monolayer. Further deposition of Sb results in the attenuation of the peak at 1.5 eV, the energy-distribution curve evolving towards the bulk Sb valence-band spectrum. These facts indicate that the feature of 1.5 eV is characteristic of the Sb overlayer at low coverages in the chemisorption regime. We can associate this peak with the nonbinding Sb bands S_5 and S_6 which run throughout the two-dimensional Brillouin zone in this energy range. These states are expected to disappear upon increasing coverage since their existence depends on the geometry and on the orbital hybridization, which are determined by the interaction with the substrate atoms.

While this assignment confirms the reliability of our calculation, further experimental work is needed to detect the other electronic states found in our results. In particular, angularly resolved experiments using appropriate photon energies could allow study of the dispersion of the *s* states, S_1 and S_2, which lie in the ionic gap.

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