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1998 J. Phys.: Condens. Matter 10 67

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# ***Ab initio* LMTO calculation of the electronic structure of an ordered monolayer of Sb on a relaxed GaAs(110) surface**

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Received 9 July 1997, in final form 9 October 1997

**Abstract.** We present electronic surface states as obtained by a comprehensive and systematic study of a monolayer of Sb on a relaxed GaAs(110) zinc-blende surface using the first-principles full-potential self-consistent linear muffin tin orbital (LMTO) method. By considering the well accepted epitaxial continued layer structure (ECLS) model we investigate the surface states in the fundamental band gap along high-symmetry directions of the surface Brillouin zone. For the ordered overlayer Sb/GaAs(110), intrinsic surface states appear in the energy gap region which shift towards the bulk valence and the conduction band region when the relaxations of the surface atoms are considered. A detailed analysis of the surface and resonance states reveals that they are in excellent agreement with the available experimental data and the existing pseudopotential calculations.

## **1. Introduction**

The adsorption of metal atoms on compound semiconductor surfaces has great practical importance in Schottky barrier formation at metal–semiconductor interfaces. In fact, the growth of multi-layer heterojunction systems and mechanisms of Schottky barrier formation, Fermi level pinning and band bending can be well understood by considering adsorption of metal on semiconductor surfaces.

The adsorption of Sb on the GaAs(110) surface has been studied extensively by various workers, assuming different atomic geometries. On the experimental side scanning tunnelling microscopy (STM) measurements were performed by Feenstra and Martensson (1988), Feenstra *et al* (1989) and Martensson and Feenstra (1989). Moreover, LEED (Duke *et al* 1982, Ford *et al* 1990), and XSW (Kendelewicz *et al* 1992) experiments measured the atomic and electronic structure of the Sb/GaAs interface.

Among all the proposed geometries the most widely accepted geometry is the epitaxial continued layer structure (ECLS). It was proposed by Swarts *et al* (1982) by assuming that the adsorbed metallic Sb atoms occupy the next lattice layer on a nearly unrelaxed GaAs(110) surface. The Sb chains bridge the GaAs chains of an unrelaxed surface. Therefore, it is often called the bridge chain model.

On the other hand, the early work by Skeath and his co-workers (Skeath *et al* 1980, 1981, 1983) using LEED and photoemission experiments showed that room-temperature deposition of one monolayer (1 ML) of Sb on GaAs(110) reveals a stable and ordered adsorbate structure. They suggested a  $p^3$  structure model where the adsorbate Sb atom forms a chain similar to that of Ga and As atoms. It was further noted that every second

Sb atom is strongly bound to a Ga atom, donating two p electrons into the empty p-type dangling orbital of Ga and one p-type electron into an Sb–Sb bond orbital. The Sb s-type electrons remain in a tightly bound lone-pair orbital.

STM studies have been interpreted using the ECLS as well as the epitaxial on-top structure (EOTS) model by LaFemina *et al* (1990). They suggested that the EOTS model gives a better fit to the data than the ECLS model and that the proposed  $p^3$  structure is only marginally inconsistent with the experimental data, but LEED (Ford *et al* 1990) and XSW (Kendelewicz *et al* 1992) measurements have strongly supported the ECLS model.

However, many experimental results obtained by STM spectroscopy (Shih *et al* 1990), ARPES (Tulke *et al* 1986, Tulke and Luth 1986, Martensson *et al* 1986) and inverse photoemission (IP, Drube and Himpsel 1988) for the surface electronic structure strongly favour the validity of a bonding model. Core level spectroscopy (Skeath *et al* 1983, Schaffler *et al* 1987) revealed the existence of at least two chemically distinct Sb species at the surface. On the other hand, valence band photoemission spectroscopy (Skeath *et al* 1980, 1981) discovered Sb-induced surface states just below the GaAs valence band maximum (VBM).

Surface sensitive high-resolution electron energy loss spectroscopy (HREELS) measurements (Mariani *et al* 1989, Annovi *et al* 1990, Betti *et al* 1992) on the Sb adsorbed GaAs system grown at room temperature exist, but the conclusions about the interface are rather limited. Recent HREELS has revealed a low-energy surface state transition around 1.55 eV.

On the theoretical side, various groups have calculated the surface electronic structure of the Sb/GaAs system using different methods. Bertoni *et al* (1983) performed a self-consistent pseudopotential calculation without using equilibrium relaxed geometry while Mailhiot *et al* (1985) employed an empirical tight-binding calculation for an energy minimized surface geometry of the same type. LaFemina *et al* (1990) identified two new minimum-energy surface structures using a tight-binding total energy formalism. The atomic geometry and electronic structure of a monolayer of Sb on the (110) GaAs surface was also studied by Srivastava (1993) using *ab initio* molecular dynamics. Schmidt *et al* (1994) investigated chemisorption of Sb on the relaxed GaAs(110) surface using density functional theory (DFT) within the local density approximation (LDA) and norm-conserving fully separable *ab initio* pseudopotentials. Recently, Magri (1996) studied the electronic properties of Sb deposited on GaAs(110) in the submonolayer-coverage regime using the self-consistent first-principles pseudopotential method.

The application of the pseudopotential–DFT calculations has its own limitations. About three-quarters of the elements of the periodic table have quite strong pseudopotentials and the remaining one-quarter of the atoms have weak pseudopotentials to permit expansion of the pseudo-wave-functions in plane waves. Even for this one-quarter of the atoms, the problem of slow convergence of the plane wave basis limits the choice of the number of atoms in the supercell. In the linear augmented plane wave method one again chooses a large basis. Thus, the most economical basis functions are seen to be the linear muffin tin orbitals (LMTOs).

Usually in the application of the standard LMTO method, an atomic sphere approximation (ASA) is used to make it efficient. However, this LMTO–ASA method suffers from several disadvantages. (i) It neglects the symmetry breaking terms by discarding the non-spherical parts of the electron density. (ii) The method discards the interstitial region by replacing the muffin tin spheres by space filling Wigner spheres. (iii) It uses spherical Hankel functions with vanishing kinetic energy only. The present LMTO method (Methfessel 1988, Agrawal *et al* 1992) goes beyond the LMTO method employed usually in

the ASA. However, in the present method the calculation of atomic forces is very difficult and has not been done.

The above-mentioned experimental and theoretical studies lead to the conclusion that the ECLS model is the energetically most favourable geometrical model.

In this paper we present a comprehensive and systematic study of the electronic band structure of the Sb adsorbed on GaAs(110) zinc-blende surface by employing the first-principles full-potential self-consistent LMTO method. We have investigated the surface and resonance states in some symmetry directions of the surface Brillouin zone and compare them with the available experimental data. We find that they are in excellent agreement with the experimental data and with the results of pseudopotential calculations, especially in the valence band region. Occupied as well as unoccupied Sb derived surface states appear in the fundamental energy gap for the relaxed Sb/GaAs(110) surface.

## 2. Method

For detailed information about the LMTO method used, we refer to earlier articles (Agrawal and Agrawal 1992, Agrawal *et al* 1994, Agrawal and Agrawal 1993, 1994, Methfessel 1988).

Scalar relativistic versions were performed in all the calculations. The LMTO envelope functions were formed from the spherical harmonic components having  $l \leq 4$  with three decay energies,  $-0.01$ ,  $-1.0$  and  $-2.3$  Ryd inside the muffin tin spheres for the occupied atomic sites and with two decays given by  $-0.7$  and  $-1.0$  Ryd for the interstitial region. The surface states should decay quite fast, especially towards the vacuum side. Thus, high values for the decay factor have been chosen in the calculations. The local density potential of Hedin and Lundqvist (1971) has been utilized. The LMTO basis functions in the valence energy region were chosen as Ga (4s,4p,4d), As (4s,4p,4d) and Sb (5s,5p,5d).

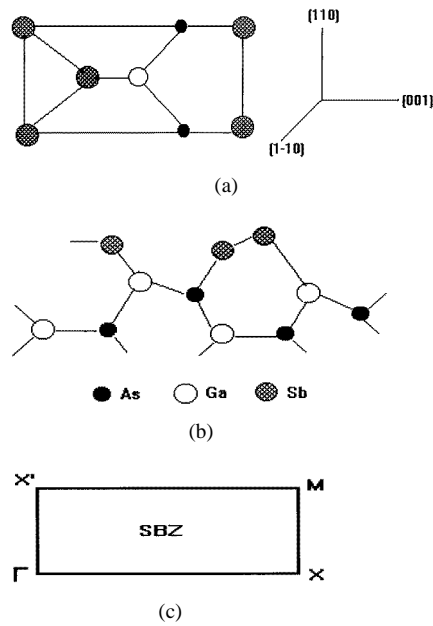
Empty spheres were assumed to be present at the vacant sites and a set of appropriate s, p, d states were chosen for them. The core electrons are not frozen but are relaxed in the sense that the core electron charge density is recalculated in each iteration in the self-consistent loop. We have not considered the spin-orbital coupling but have generated the self-consistent supercell potentials by considering the scalar relativistic effects. It has been observed that spin-orbit coupling to lowest order splits only the bands and does not change the relative position of band centres. The cohesive properties are hardly affected.

## 3. Calculations

### 3.1. Bulk superlattice

The present calculation starts from the ideal geometry, and the self-consistent LMTO calculations were carried out until the electron charge density was self-consistent. Figures 1(a) and (b) shows the top view and the side view respectively of the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface.

We have computed the electronic structure of a 14-layer bulk superlattice by repeating a supercell containing 56 atoms on a lattice. Out of the 56 atoms in the supercell, 28 are real and 28 are empty spheres to fill the vacant interstitial space. The Gaussian broadening is chosen to be 0.015 Ryd. For the bulk slab, the minimum energy appears at a lattice parameter equal to 5.54 Å which is very close to the experimental value of 5.653 Å for GaAs. The discrepancy for the lattice parameter is of the order of 1.82%.



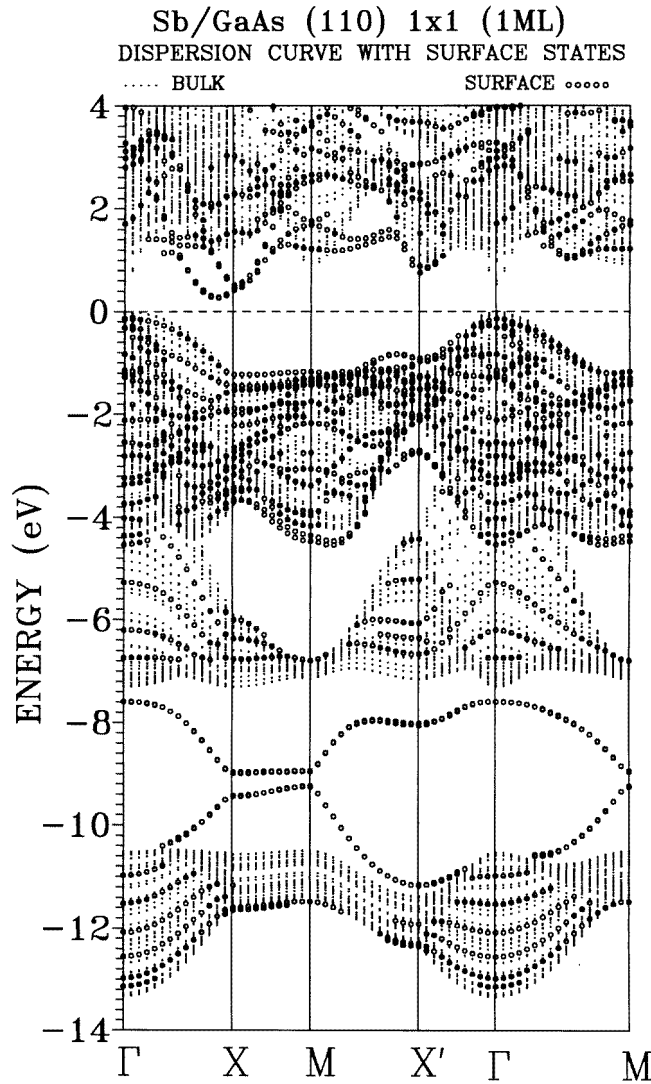
**Figure 1.** The surface unit cell of the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface: (a) top view; (b) side view; (c) the surface Brillouin zone.

### 3.2. Sb/GaAs (110) $1 \times 1$ (1 ML) surface

We use a nine-layer slab containing surfaces at both ends. The selection of nine layers is sufficient for accuracy with respect to surface state energy and states (Chelikowsky and Cohen 1979). Sb atoms are adsorbed on the surface layer. In order to reduce the interaction of the two end surfaces we have created a vacuum region having extension equivalent to three layers for each surface, i.e., a vacuum region equivalent to six layers between two slabs. A similar vacuum region for the electronic structure has been used by a number of other workers (Schmidt *et al* 1994, Zunger 1980, Alves *et al* 1991). The translational invariance of the surface is preserved in the two directions parallel to the surface (i.e.  $x$ - and  $y$ -directions) while in the  $z$ -direction we have formed a superlattice consisting of the GaAs slab and vacuum region, alternately.  $x$  is taken parallel to the direction of the chains (1–10),  $y$  is parallel to (001) and  $z$  is perpendicular to the surface plane as shown in figure 1(a). The surface, being a planar defect, will induce surface states: resonance and/or localized ones which would be characterized by the decay of the wave functions as we move away from the surface defect on either side.

At first, the calculations were performed for the perfect Sb/GaAs(110) surface, allowing relaxation between the surface layer and the underneath layer but without making any change in the interspacing of the remaining bulk layers. The minimum-energy configuration is obtained for a 3.8% dilation of the underlayer from the surface layer along the (110) direction.

For the perfect Sb/GaAs surface, intrinsic surface states appear in the fundamental energy gap region which shift towards the bulk valence and the conduction band region when the relaxation of the surface atoms is considered. For the calculation of the relaxed Sb/GaAs(110) surface geometry, the positions of the atoms of the surface and the two underlayers as reported by Srivastava (1992) were employed.

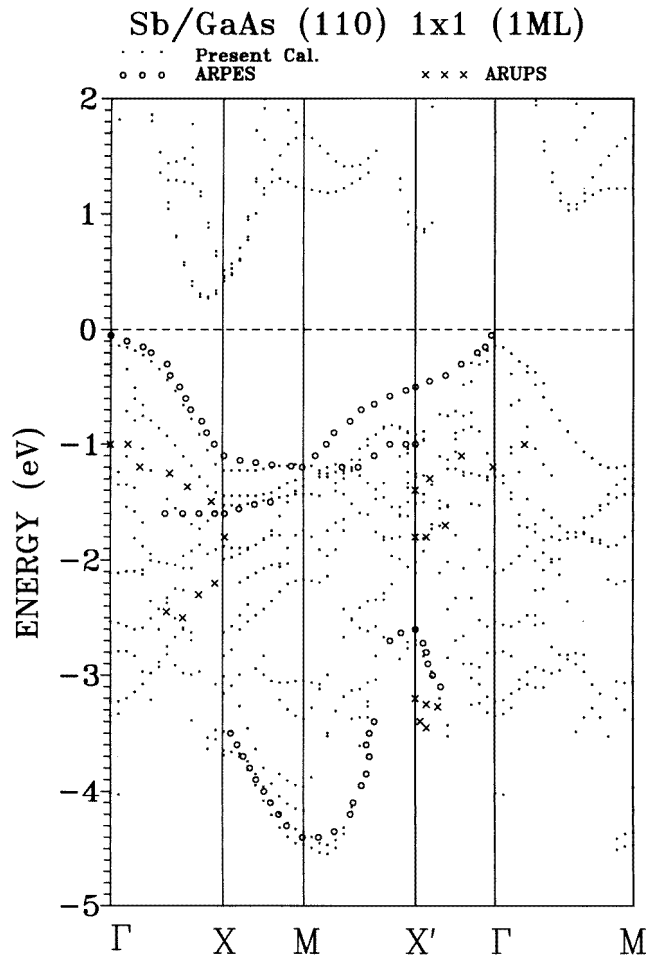


**Figure 2.** A comparison of the band structure for GaAs in the bulk with the Sb/GaAs(110)  $1 \times 1$  (1 ML) relaxed surface.

## 4. Results and discussion

### 4.1. Surface band structure

We have chosen a mesh of selected 18  $k$ -points in the irreducible part of the surface Brillouin zone to achieve self-consistency. The surface Brillouin zone is shown in figure 1(c). The symmetric points of the surface Brillouin zone are  $\Gamma$  (0, 0, 0), X (0.5, -0.5, 0.0), M (0.5, -0.5, 0.5) and X' (0, 0, 0.5) and they lie in the  $k$ -plane parallel to the surface (110). The surface states are determined by identifying those states for which the square of the modulus of the eigenvector calculated on the muffin-tin spheres decreases as one moves away from the layer underneath to the surface layer. In figure 2, we have depicted

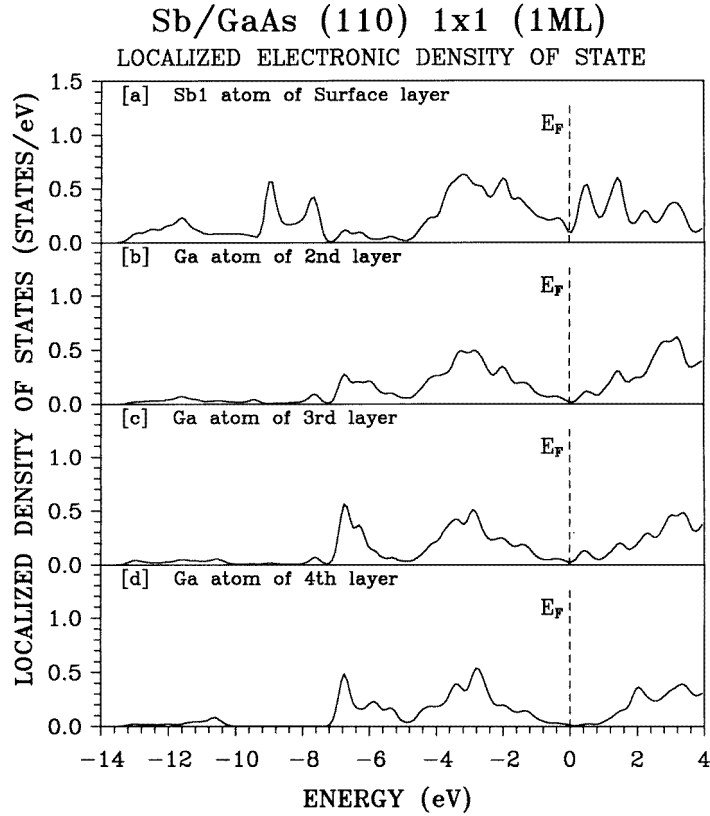


**Figure 3.** A comparison of the presently calculated dispersion curves with the experimental data from ARPES (Martensson *et al* 1986) and ARUPS (Tulke *et al* 1986).

all those surface states for which the square of the modulus of the eigenvector decreases by 36% or more. These states are mainly localized on the surface layer and/or on the underneath layer. We have employed the Mullikan decomposition technique to determine the magnitudes of the wave functions at the different lattice sites occupied by the real atoms. A similar procedure has been adopted by Fiorentini *et al* (1993).

In figure 2, we show the dispersion of the surface as well as the resonance bound states along high-symmetry lines in the surface Brillouin zone together with the bulk band structure projected onto the (110) plane. Sb-derived occupied and empty surface states appear in the neighbourhood of the fundamental gap of the projected band structure and they are well separated energetically. There are two types of Sb atom in the monolayer of Sb on the GaAs(110) surface. One of them is Sb coupled to the Ga atom, called Sb1, whereas the other one, which is coupled to the As atom, is named here Sb2.

The Sb-induced surface states have more nearly  $p_z$  character normal to the Sb-Sb plane which appears in the neighbourhood of the conduction band and penetrate into the energy

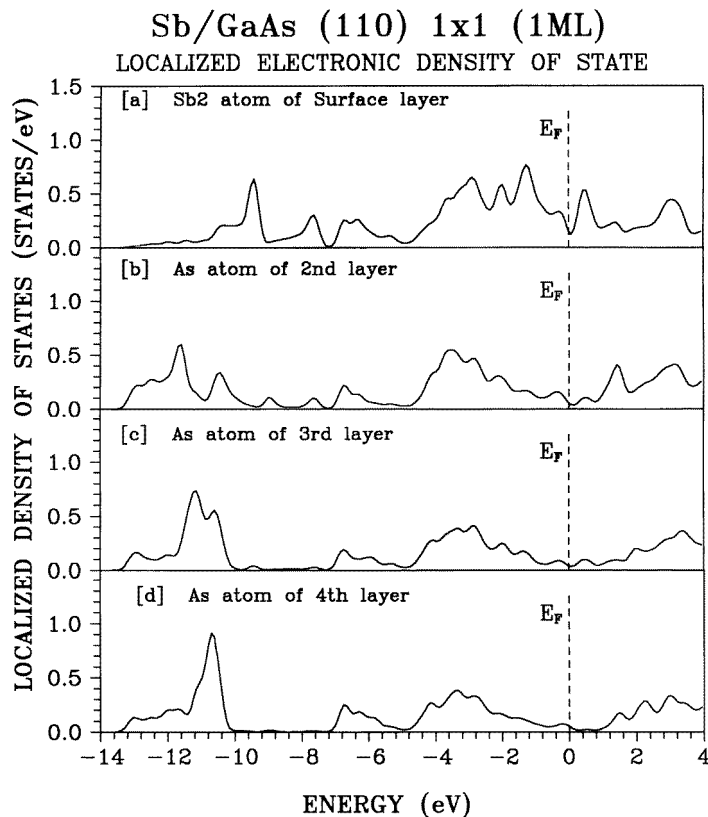


**Figure 4.** The localized density of states for Sb coupled to the Ga atoms in the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface.

gap. However, these  $\pi$  antibonding states are likely to be raised after the inclusion of the many-body effects not included in the present paper. The interpretation of the energy locations of the two unoccupied conduction band states is somewhat complicated because of the limitations of the LDA theory where the on-site correlation effects have been ignored. In the present system they seem to be characterized by the occurrence of high electron densities between Sb and the substrate atoms and are the results of the mixing of the Sb  $p_\pi$  states with the dangling orbitals of the substrate atoms. We find that these surface states show downward dispersion in the  $\Gamma$ -X- and  $\Gamma$ -X'-symmetry directions. They penetrate into the conduction band of the bulk band structure at the M-symmetry-point, thus showing a resonant behaviour.

The Sb-induced states also appear in the fundamental gap near the top of the valence band. These states are the bonding combinations of the very  $p_z$ -like orbitals of the Sb and the substrate atoms. We also find that these p-like states are not only localized at Sb atoms: rather they have quite significant contributions from the substrate Ga and As atoms. These surface states which appear along the X-M-X'-direction of the surface Brillouin zone are well localized and show a resonance behaviour near the  $\Gamma$ -point. A flat band character is seen between the X- and M-symmetry-points. This couple of bands can be identified as due to lone pairs of the Sb atoms, since they accommodate two p electrons.





**Figure 5.** The localized density of states for Sb coupled to the As atoms in the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface.

In the stomach gap of the bulk band structure at energy  $-4.35$  eV near the M-symmetry-point, two localized surface states appear. They belong to bonding combinations of Sb  $p_\sigma$ -like states with As and Ga  $sp^3$  dangling hybrids. A strong downward dispersion appears along X–M- and X'–M-directions. It has a strong surface character except near the surface Brillouin zone centre.

In the lower part of the stomach gap near  $-6.79$  eV at the M-symmetry-point, a cation-derived surface state appears, which shows again a downward dispersion along X–M- and X'–M-directions. This state possesses s-type character. We notice that in other theoretical calculations this very state appears in the ionic gap. Resonance surface states appear also in the energy region  $-4.0$  to  $-7.0$  eV.

In the ionic gap of the bulk band structure between  $-8.0$  and  $-10.0$  eV there are two Sb-derived localized surface states. They are almost localized at one of the two differently bonded Sb atoms. The states near  $-8.0$  and  $-10.0$  eV are localized on Sb2 and Sb1 atoms, respectively. The orbital characters are essentially s-like. These surface states are flat and nearly degenerate in the X–M direction. Similar conclusions have been drawn by Srivastava (1993) and Schmidt *et al* (1994).

At the bottom of the valence band, a localized anion- (As-) derived surface state appears which has mainly s-type character. This state shows a resonant behaviour along  $\Gamma$ –X- and

**Table 1.** A comparison of the calculated surface states with the available experimental data and other calculations at the  $\Gamma$ -symmetry-point in the surface Brillouin zone of the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface. All energies are in electron volts.

Surface states	Present calculation	Experimental data	Other calculations
$\Gamma_1$	1.71	2.1 <sup>a</sup>	1.8 <sup>b</sup> , 1.9 <sup>c</sup> , 1.9 <sup>d</sup>
$\Gamma_2$	-0.14		-0.1 <sup>d</sup> , -0.1 <sup>c</sup>
$\Gamma_3$	-0.83, -1.15	-1.0 <sup>e</sup>	-1.0 <sup>c</sup> , -1.08 <sup>d</sup>
$\Gamma_4$	-2.53		-2.5 <sup>d</sup> , -2.5 <sup>c</sup>
$\Gamma_5$	-3.23, -3.35		-3.4 <sup>d</sup> , -3.4 <sup>c</sup>
$\Gamma_6$	-7.59		-7.0 <sup>f</sup> , -7.6 <sup>c</sup> , -7.8 <sup>d</sup>
$\Gamma_7$			-10.2 <sup>d</sup> , -10.2 <sup>c</sup>
$\Gamma_8$	-12.98		-12.8 <sup>d</sup> , -12.8 <sup>c</sup>

<sup>a</sup> Inverse photoemission, Drube and Himpsel (1988).

<sup>b</sup> *ab initio* molecular dynamics–DFT, Srivastava (1993).

<sup>c</sup> Tight binding total energy formalism, LaFemina *et al* (1990).

<sup>d</sup> Tight binding calculation, Mailhiot *et al* (1985).

<sup>e</sup> Angle resolved ultra violet photoemission spectroscopy, Tulke *et al* (1986).

<sup>f</sup> *ab initio* pseudopotential, Schmidt *et al* (1994).

$X'$ – $\Gamma$ -directions but is a well localized surface state along the  $X$ – $M$ – $X'$ -direction. However, we notice that these surface states have slow-decaying behaviour in comparison to other surface states.

We compare the present results for the dispersion curves with the data available from the angle-resolved photo-emission spectroscopy (ARPES) and angle-resolved UV photo-emission spectroscopy (ARUPS) experiments in figure 3. For clarity in figure 3, we have plotted those surface states for which the value of the squared eigenvector decays by 64% on the underneath GaAs layer. The calculated surface states at the principal symmetry points along with the available experimental data and the results of other calculations are included in tables 1–4. The experimentally measured surface states lying near the top of the valence band are in excellent agreement with the present values at the symmetry points  $\Gamma$ ,  $X$  and  $M$ . The calculated values are smaller than the experimental ones at the symmetry point  $X'$  by about  $-0.4$  eV. The measured values in the energy region  $-1.0$  to  $-3.0$  eV are seen to be present in the calculated dispersion curves. The calculated dispersion of the Sb-induced surface states lying in the upper part of the stomach gap around  $-4.0$  eV is in excellent agreement with the experimental data available mainly in the  $X$ -,  $M$ - and  $X'$ -symmetry directions. In fact, our results are closer to the experimental values than the results of other theoretical calculations (Srivastava 1993, Schmidt *et al* 1994). It may be noted that in the present calculation the correlation scheme of Hedin and Lundqvist (1971) has been employed whereas Srivastava (1993) and Schmidt *et al* (1994) have used a different correlation scheme, namely that of Ceperley and Alder (1980). So far no experimental measurement is available for the surface states observed in the ionic or heteropolar gap region.

The summary of the tables reveals that most of the energies are seen to be in good agreement with the presently calculated surface states. The presently calculated surface states are in better agreement with the experimental values in the upper part of the valence band region than other theoretical calculations as shown in table 2. In the lower region of the valence band they are fairly consistent with the values of other workers. At the symmetry point  $M$  (table 3), the calculated values are in excellent agreement with the experimental

**Table 2.** A comparison of the calculated surface states with the available experimental data and other calculations at the X-symmetry-point in the surface Brillouin zone of the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface. All energies are in electron volts.

Surface states	Present calculation	Experimental data	Other calculations
X <sub>1</sub>	0.42, 0.51		1.0 <sup>a</sup> , 1.0 <sup>b</sup> , 1.6 <sup>c</sup> , 1.8 <sup>d</sup>
X <sub>2</sub>	-1.23	-1.10 <sup>e</sup>	-0.5 <sup>a</sup> , -0.8 <sup>c</sup> , -0.8 <sup>d</sup> , -0.8 <sup>b</sup>
X <sub>3</sub>	-1.44		-1.25 <sup>d</sup> , -1.3 <sup>b</sup>
X <sub>4</sub>	-1.53	-1.6 <sup>e</sup>	
X <sub>5</sub>	-1.88	-1.8 <sup>f</sup>	
X <sub>6</sub>	-2.63, -2.83		-2.96 <sup>e</sup>
X <sub>7</sub>	-3.01, -3.20, -3.48		-3.12 <sup>c</sup> , -3.20 <sup>d</sup> , -3.5 <sup>a</sup>
X <sub>8</sub>	-8.96		-8.0 <sup>a</sup> , -8.6 <sup>d</sup> , -8.64 <sup>c</sup>
X <sub>9</sub>	-9.44		-8.50 <sup>a</sup> , -9.4 <sup>d</sup> , -9.44 <sup>c</sup>
X <sub>10</sub>	-11.64		-11.0 <sup>a</sup> , -11.2 <sup>c</sup> , -11.4 <sup>c</sup>

<sup>a</sup> *ab initio* pseudopotential, Schmidt *et al* (1994).

<sup>b</sup> *ab initio* molecular dynamics–DFT, Srivastava (1993).

<sup>c</sup> Tight binding total energy formalism, LaFemina *et al* (1990).

<sup>d</sup> Tight binding calculation, Mailhiot *et al* (1985).

<sup>e</sup> Angle resolved photoemission spectroscopy, Martensson *et al* (1986).

<sup>f</sup> Angle resolved ultra violet photoemission spectroscopy, Tulke *et al* (1986).

**Table 3.** A comparison of the calculated surface states with the available experimental data and other calculations at the M-symmetry-point in the surface Brillouin zone of the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface. All energies are in electron volts.

Surface states	Present calculation	Experimental data	Other calculations
M <sub>1</sub>	1.22		1.4 <sup>a</sup> , 1.96 <sup>b</sup> , 2.3 <sup>c</sup> , 2.4 <sup>d</sup>
M <sub>2</sub>	-1.17	-1.2 <sup>e</sup>	-0.8 <sup>b</sup> , -0.9 <sup>a</sup> , -0.9 <sup>c</sup> , -1.0 <sup>d</sup>
M <sub>3</sub>	-1.29		-1.12 <sup>b</sup> , -1.2 <sup>a</sup> , -1.3 <sup>c</sup>
M <sub>4</sub>	-3.10		-2.96 <sup>b</sup> , -3.0 <sup>a</sup>
M <sub>5</sub>	-3.38		-3.28 <sup>b</sup> , -3.40 <sup>a</sup>
M <sub>6</sub>	-4.35, -4.46	-4.4 <sup>c</sup>	-4.0 <sup>d</sup> , -4.1 <sup>d</sup> , -4.1 <sup>c</sup>
M <sub>7</sub>	-8.95		-8.0 <sup>d</sup> , -8.64 <sup>b</sup> , -8.8 <sup>a</sup>
M <sub>8</sub>	-9.25		-8.30 <sup>d</sup> , -9.44 <sup>b</sup> , -9.5 <sup>a</sup>
M <sub>9</sub>	-11.48		-10.5 <sup>d</sup> , -11.2 <sup>b</sup> , -11.3 <sup>a</sup>

<sup>a</sup> Tight binding calculation, Mailhiot *et al* (1985).

<sup>b</sup> Tight binding total emission formalism, LaFemina *et al* (1990).

<sup>c</sup> *ab initio* molecular dynamics–DFT, Srivastava (1993).

<sup>d</sup> *ab initio* pseudopotential, Schmidt *et al* (1994).

<sup>e</sup> Angle resolved photoemission spectroscopy, Martensson *et al* (1986).

values than other theoretical calculations. Small discrepancies similar to those of other workers are seen in the symmetry direction  $X'–\Gamma$  (table 4).

#### 4.2. Electronic density of states

The electronic density of states is an important factor which allows one to establish the exact nature of the surface states with respect to different layers. Here, the Gaussian broadening is chosen to be 0.015 Ryd.

**Table 4.** A comparison of the calculated surface states with the available experimental data and other calculations at the  $X'$ -symmetry-point in the surface Brillouin zone of the Sb/GaAs(110)  $1 \times 1$  (1 ML) surface. All energies are in electron volts.

Surface states	Present calculation	Experimental data	Other calculations
$X'_1$	0.76, 0.88		1.76 <sup>a</sup> , 1.8 <sup>b</sup> , 1.8 <sup>c</sup> , 2.0 <sup>d</sup>
$X'_2$	-0.91	-0.5 <sup>e</sup> , -1.4 <sup>f</sup>	-0.3 <sup>d</sup> , -0.5 <sup>c</sup> , -0.6 <sup>b</sup> , -0.64 <sup>a</sup>
$X'_3$	-1.25	-1.0 <sup>e</sup>	-1.1 <sup>b,c</sup> , -1.28 <sup>a</sup>
$X'_4$	-2.11	-1.8 <sup>f</sup> , -2.6 <sup>e</sup>	-2.0 <sup>a,b,d</sup>
$X'_5$	-2.70	-3.2 <sup>f</sup> , -3.4 <sup>f</sup>	-2.4 <sup>b,d</sup> , -2.48 <sup>a</sup>
$X'_6$	-8.01		-7.2 <sup>b</sup> , -7.28 <sup>a</sup> , -7.4 <sup>d</sup>
$X'_7$	-11.15		-10.4 <sup>d</sup> , -11.0 <sup>b</sup> , -11.10 <sup>a</sup>
$X'_8$	-12.35		-11.5 <sup>d</sup> , -12.2 <sup>b</sup> , -12.7 <sup>a</sup>

<sup>a</sup> Tight binding total emission formalism, LaFemina *et al* (1990).

<sup>b</sup> Tight binding calculation, Mailhiot *et al* (1985).

<sup>c</sup> *ab initio* molecular dynamics–DFT, Srivastava (1993).

<sup>d</sup> *ab initio* pseudopotential, Schmidt *et al* (1994).

<sup>e</sup> Angle resolved photoemission spectroscopy, Martensson *et al* (1986).

<sup>f</sup> Angle resolved ultra violet photoemission spectroscopy, Tulke *et al* (1986).

The localized densities of states for the different layers for Sb, Ga and As atoms are shown in figures 4 and 5. In figures 4(a) and 5(a) we observe that the magnitudes of Sb-derived states are very prominent in the neighbourhood of the band gap. Sb-derived states are also very dominant in the  $-7.0$  to  $-10.0$  eV region. A high density of surface states appears at the substrate As atoms near the bottom of the valence band around  $-12.0$  eV. In figure 4(b)–(d) and in figure 5(b)–(d) we have shown the density of states for Ga and As atoms for different layers, respectively. We find that the density of surface states decays as one moves towards the middle of the slab.

The Sb1- and Sb2-induced states appearing in the energy gap or its neighbourhood are localized mainly on the Sb monolayer. There are only small contributions from the Ga atoms lying in the next layer. The same is true for the Sb-induced s-type states lying in the ionic gap (see figure 4). The two extra electrons of As atoms lying on the substrate layer occupy the surface states just below the top of the valence band.

## 5. Conclusions

The electronic band structure of an ordered monolayer of Sb on a relaxed GaAs(110) zinc-blende surface has been investigated by employing the first-principles full-potential self-consistent linear muffin tin orbital (LMTO) method. We have investigated the intrinsic surface states in the fundamental gap, stomach gap and ionic gap of the system of Sb adsorbed on GaAs(110) at principal symmetry points of the surface Brillouin zone. We have also studied the density of states for Sb, Ga and As atoms for different layers. A detailed analysis of the surface and resonance states is seen to be in excellent agreement with the available experimental data and other theoretical calculations.

## Acknowledgments

All the calculations were performed on HP 735 and HP 720 computer systems available in our laboratory. The authors are grateful to the University Grants Commission, New Delhi, and the Department of Science and Technology, New Delhi, for financial assistance.

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