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Tight-binding calculation of the electronic states of bulk-terminated GaAs(311)A and B surfaces*

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We have carried out theoretical investigations on the electronic structure of GaAs(311)A and GaAs(311)B surfaces. The bulk electronic structure of GaAs has been described by the second-neighbour tight-binding formalism and the surface electronic structure was evaluated via an analytic Green function method. First, we present the surface band structure together with the projected bulk band of both Ga-terminated and As-terminated for GaAs(311)A and GaAs(311)B surfaces, respectively. In each case, the number of surface states is determined, and the localized surface features and orbital properties of these surface states along Γ–Y–S–X–Γ high symmetry lines of the surface Brillouin zone are discussed. For the Ga-terminated GaAs(311)A (1×1) surface, we have tested two possible structure models, i.e. "the bridge site" and "the hollow site" models. In comparison with the angle-resolved photoelectron spectroscopy studied recently, the results have shown that the surface electronic states of the hollow site model are in good agreement with the experiments, whereas those of the bridge site model are not. So we have concluded that the hollow site model is favourable for the Ga-terminated GaAs(311) (1×1) surface and the bridge site model should be excluded.

Keywords: tight-binding calculation, high-index crystal surface, surface states, resonance states
PACC: 7320, 6188

1. Introduction

The high Miller index surfaces of III–V compound semiconductors have received considerable attention because of their attractive heterostructure properties grown along this direction. For instance, the GaAs(311) surface allows for growth of high-quality p-type materials by using Si dopants, thereby eliminating many of the problems encountered with other acceptors that have to be used for (100) surfaces.[1−5] Furthermore, owing to the non-(100)-orientation and the different planar projections of the conduction and valence bands in the constituent crystal, the optical and vibrational properties of the heterostructures grown in the (311) direction have been a subject of interest. The (311)AlAs/GaAs quantum wells and superlattices on the GaAs(311) substrate have recently been fabricated by molecular beam epitaxy.[6−10] However, with the rapidly increasing demands for smaller dimensions of solid-state devices, the nature of the underlying interface has become increasingly important. Hence, a proper understanding of the electronic properties of such surfaces is crucial.

Although all of the above-mentioned features are influenced by the detailed atomic and electronic structure of the GaAs(311) surface, the knowledge about the surface electronic and geometric structure of GaAs(311) surfaces is very limited and contributions on this subject are scarce both in experiments and theoretical studies.[11−17] This may be due to the following facts: Firstly, it is very difficult to prepare this high-index surface in experiments. Only a few experiments, such as the low-energy electron diffraction (LEED) intensity analysis, Auger electron spectroscopy (AES) and angle-resolved UV photoelectron spectroscopy (ARUPS), have been carried out. Secondly, in theoretical studies, since the high miller index surfaces are usually stepped and there are two inequivalent surfaces on each side of the supercells of the slab, the difference of the polar characters of these surfaces will turn out to be remarkable, so any *ab-initio* method employing the slab-supercell method must use a relatively large set of atoms and thus requires more time in calculation. Very recently, the theoretical investigations of GaAs(211), GaAs(114) and Si(211) surfaces have been published.[18−20] Up to now, no proper investigations on the ideal GaAs(311) surface

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have been performed. So we carry out the study of the electronic states of GaAs(311) surface.

2. Model and method of calculation

We have adopted the second-neighbour tight-binding sp^3 model to describe the bulk electronic structure. The surface electronic structures of GaAs(311) are evaluated via an analytic Green function method proposed by Pollmann *et al.*[21] This method has been successfully applied to Si, Ge and GaAs surfaces, both relaxed and reconstructed low-index, and the results are in good agreement with the ARUPS measurements. In addition, we have also obtained calculated results on the electronic structures of some high Miller index surfaces and gained good results.[22−27] Although this model is semi-empirical and the results obtained are less accurate than those of the first-principles calculation, it allows for a simple interpretation of the different bands in terms of the atomic orbital, and can give more distinct properties in some aspects, such as orbital or local properties of electronic states.

In order to calculate the surface electronic states, we have to solve the surface Green function through the Dyson equation. To do this, we first express the Green function matrix elements in an appropriate basis. Under the tight-binding formalism, we choose the linear combination of atomic orbits in each of the layers as the basis. In the so-called atom-layer-orbital representation, the matrix elements of the bulk Green function are given by

$$\begin{aligned}&\langle \boldsymbol{q}, \alpha\mu m|G_0|\boldsymbol{q}, \alpha'\mu' m'\rangle \\ =&\frac{1}{\sqrt{11}}\lim_{\varepsilon\to 0}\sum_n \int_{-\sqrt{11}/2}^{\sqrt{11}/2} \mathrm{e}^{\mathrm{i}\pi\frac{2}{\sqrt{11}}x[g(m,\mu)-g'(m',\mu')]} \\ &\times \mathrm{d}x\frac{C^{n^*}_{\alpha'\mu'm'}(\boldsymbol{q},x)\times C^n_{\alpha\mu m}(\boldsymbol{q},x)}{E+\mathrm{i}\varepsilon-E_n(\boldsymbol{q},x)}\end{aligned}$$

for the (311)A surface. $g(m,\mu)=m$ when the basis atom μ in the unit cell of the m layer is the Ga atom, and $g(m',\mu')=m'+1/4$ when μ' in the unit cell of the m' layer is the As atom. The meaning of the above equation is the same as that in Refs.[22]–[27].

Since GaAs is a polar crystal, there are two differently orientated (311) surfaces, called (311)A and (311)B. This nomenclature is selected in analogy to that used for the GaAs(111) surface. Both (311)A and (311)B surfaces are low-energy surfaces which have been successfully prepared both by molecular beam epitaxy (MBE) and by ion bombardment and annealing (IBA) methods. For the MBE-prepared GaAs(311)A surface, two completely different structure models have been proposed. The model proposed by Notzel *et al.* was based on reflection high-energy electron diffraction (RHEED) and transmission electron microscopic results. They interpreted the reconstruction as a V-grooved surface with a lateral periodicity of 3.2nm and a corrugation height of 1.02nm. The STM/RHEED study by Wassermeier *et al.*[14] also yielded a 3.2nm periodicity in the $[0\bar{1}1]$ direction, but the corrugation height was found to be 0.34nm. They proposed a model which is characterized by a dimer of the surface As atoms and is confirmed by LEED measurements and surface core level investigation using synchrotron radiation. For the GaAs(311)B surface, several authors have reported on the occurrence of the (1×1) structure and also a (2×1) reconstruction structure.[13,28] Recently, a (8×1) reconstruction, which is exactly analogous to the (8×1) reconstructed GaAs(311)A surface, has been proposed, which results from the exchange of As and Ga atoms.[29] Unlike MBE, the IBA preparation of the surfaces shows (1×1) stable structures both for GaAs(311)A and GaAs(311)B surfaces.[14−16] For the A(B) surface, the MBE-prepared surface contains more As(Ga) than that prepared by IBA. The difference amounts to more than 0.5 of a monolayer in the topmost layer.

In this paper, we limit our calculation to the (311)(1×1) pattern of GaAs(311)A and GaAs(311)B surfaces. Figures 1(a) and 1(b) show the side and the top views of the bulk truncated GaAs(311)A ideal surface, respectively. The surface unit cell of GaAs(311)A is shown with a dashed line. For the bulk truncated GaAs(311)A (1×1) surface, the surface layer contains a twofold coordinated As atom and a threefold coordinated Ga atom in each surface unit cell, and the numbers of Ga and As atoms are the same. We refer to it as the As-terminated surface. Another possible ideal cut of this surface contains a surface layer with twofold and a threefold coordinated Ga atoms, which in Fig.1(a) can be visualized by removing the As atom in the surface layer. This type of surface is referred to as the Ga-terminated surface. As for the GaAs(311)B surface, the (1×1) stable surface can be prepared both by MBE and IBA techniques. The surface atomic geometry of the ideal cut can be obtained simply by exchanging the Ga atom with the As atom

in Fig.1(a).

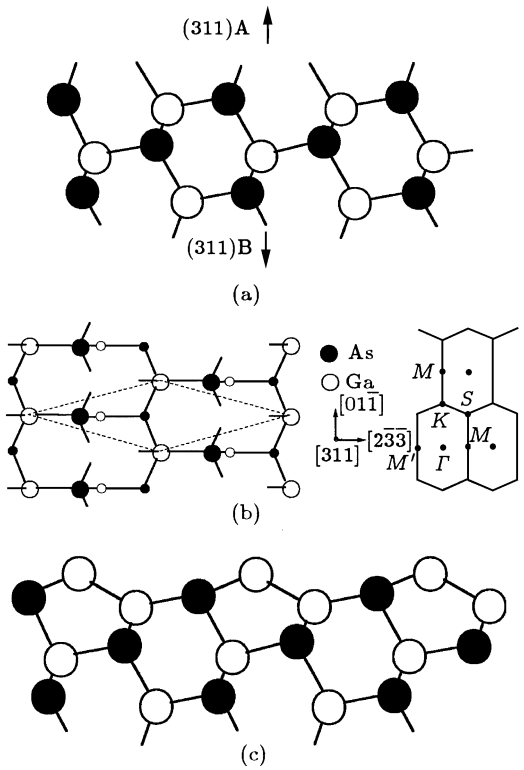


Fig.1. (a) Side and (b) top views of an ideal As-terminated (311)A (1×1) surface together with the corresponding surface Brillouin zone. The surface unit cell is marked by the dashed lines, the open circles denote the Ga atom and the solid circles denote the As atom. (c) The side view of the Ga-terminated (311)A (1×1) surface geometry (hollow site model).

3. Results and discussion

3.1. The surface band structure of the GaAs (311)A surface

Although the As-terminated GaAs(311)A surface exhibits one stable (8×1) reconstructed surface,[14] to calculate the electronic states of such a complex surface is impossible. Here, we describe the surface electronic structure of an ideal bulk-truncated GaAs (311)A (1×1) surface, which is helpful for understanding such a (8×1) reconstructed surface and serves as a very important stepping stone for investigations of reconstructed surfaces. We present the surface band structure along the high symmetric lines Γ–M–S–K–Γ of the surface Brillouin zone (SBZ) in Fig.2. The high symmetric points of the SBZ are Γ(0.0,0.0), M(0.0, 0.4264), S(0.6428, 0.4264) and K(0.7714,0.0) (units in 2π/a). The point pattern gives the bulk bands projected onto the (311) plane and the point density gives a visual impression of the density of bulk states for a given point in the SBZ. The dashed line represents the surface bound states in the gaps and the surface resonance states in the point pattern. Unlike the low-index surface of (100), the (311) surface has only one main pocket, in which the energy regions in the two-dimensional SBZ have no projected bulk bands, in the region of the bulk valence bands. The pocket is located in the region from −5.5eV to −3.0eV below the valence band maximum (VBM) along the M–S–K lines; we call this region a stomach gap. Since the stomach gap is small, most of the surface features are in resonance in this energy region.

From the investigation of the electronic structure of the As-terminated (311)A geometries, we immediately notice the three dangling bonds, i.e. one on the terrace atom and two on the edge atom. It is reasonable to expect each of these bonds to give rise to a surface state in, or very close to, the fundamental gap. The calculations also confirm this. By investigating the atomic resolved densities of states at a special point in the SBZ, we are able to assign the bonds as follows. (1) The two topmost surface states, S_1 and S_2, stem from the dangling bonds of the terrace atom and the edge atom in the surface layer, respectively. These surface states are highly localized in the surface layer. The S_1 state disperses downwards by a 1.5eV bandwidth along the M–S line and upwards by the same value along the K–Γ line. The S_2 state is at the energy level 0.6eV above the VBM and has almost no dispersion. (2) At the bottom of the fundamental gap, the surface state S_3 is found. Between M and K, this surface state is a proper surface state, however it moves down below the valence band edge and is turned into a surface resonance state along the Γ–M and K–Γ lines. (3) In the lowest area of the stomach, a few tenths of an electron volt above the edge of the projected bulk states around the stomach, we find a surface state S_4 which is interpreted as being connected to the back bonds of the Ga atom in the surface layer and the As atom in the sublayer. We called this surface state a back-bond state. (4) Crossing the heteropolar gap, the relative weight of the Ga atom density of states become negligible, and this area is completely dominated by the s-states of the As atom. The S_5 state is found just 0.9eV above the lowest part of the projected bulk states. This state directly stems from the s-orbital of the As atom in the surface layer. Along the Γ–M–S–K–Γ lines, this state has nearly no dispersion.

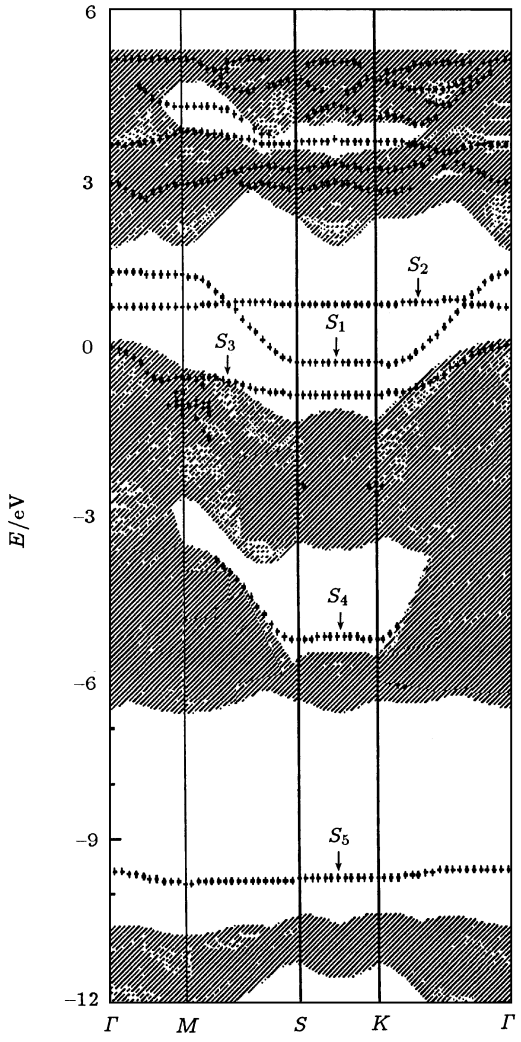


Fig.2. Electronic structure of an ideal As-terminated GaAs(311)A (1×1) surface together with the projected bulk bands. The VBM is taken to be zero energy.

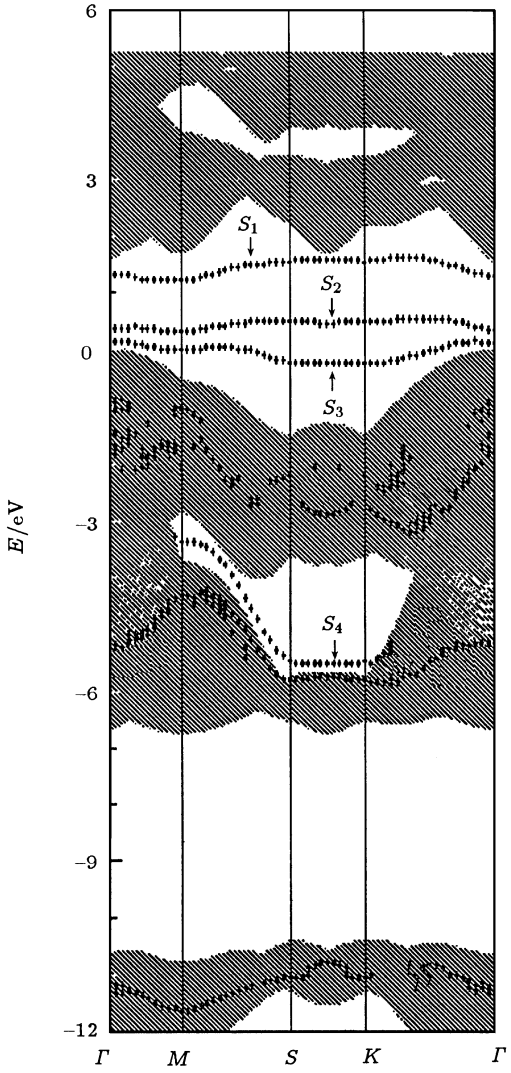


Fig.3. Electronic structure of an ideal Ga-terminated GaAs(311)A (1×1) surface together with the projected bulk bands. The VBM is taken to be zero energy.

We turn to another ideal cut of the GaAs (311)A (1×1) surface, namely the Ga-terminated surface. In this case, the surface layer contains twofold and threefold coordinated Ga atoms. From the LEED and previous theoretical studies, it was found that this surface is stable.[11,12,15,16] Two distinct structure models were considered with the Ga atoms in the surface layer, either in a twofold coordinated bridge position or in a hollow site with the Ga atoms relaxed downwards and bonding to the Ga atoms in the sublayer. The geometry of the hollow site model is indicated in Fig.1(c). In our calculation, as to the geometry of hollow site model, we have adopted a simple way of making only the topmost Ga atoms relax downwards and the other atoms remain in their bulk position. The nearest-neighbour bond length between the Ga atoms and the Ga atoms in the sublayer is assumed to be approximately the sum of the covalent radii. The distance of the Ga atoms from the second-neighbouring atoms keeps the bulk value. The results are in good agreement with the LEED experiments and the previous theoretical studies. As for the bridge site geometry, we adopt the results of the LEED study.[11,12] Upon relaxation, the toplayer twofold Ga atom moves downwards by 0.002nm from its bulk-terminated position. In the sublayer, the threefold Ga atom relaxes inwards by 0.045nm and moves by 0.04nm along the $[2\overline{3}\,\overline{3}]$ direction. To describe the change of the interaction between the atoms, we employ the empirical d^{-2} scaling law suggested by Harrison *et al.*, where d is the bond length. We plot the surface band structure of the ideal bulk terminated atoms in Fig.3, from which we once again find five

surface states; three are located in the fundamental gap, of which the topmost two, S_1 and S_2, have the same dispersion, corresponding to the dangling-bond states. The surface state S_3 stems from the change of the bond between the Ga atom in the surface and the As atom in the sublayer. The surface state S_4, which is very close to the bottom of the stomach gap, comes from the s states of the Ga atom and the p states of the As atom in the sublayer. In addition, one surface resonance state, in the bottom of the s-like projected bands, is connected to the s state of the anions in the second and third layers.

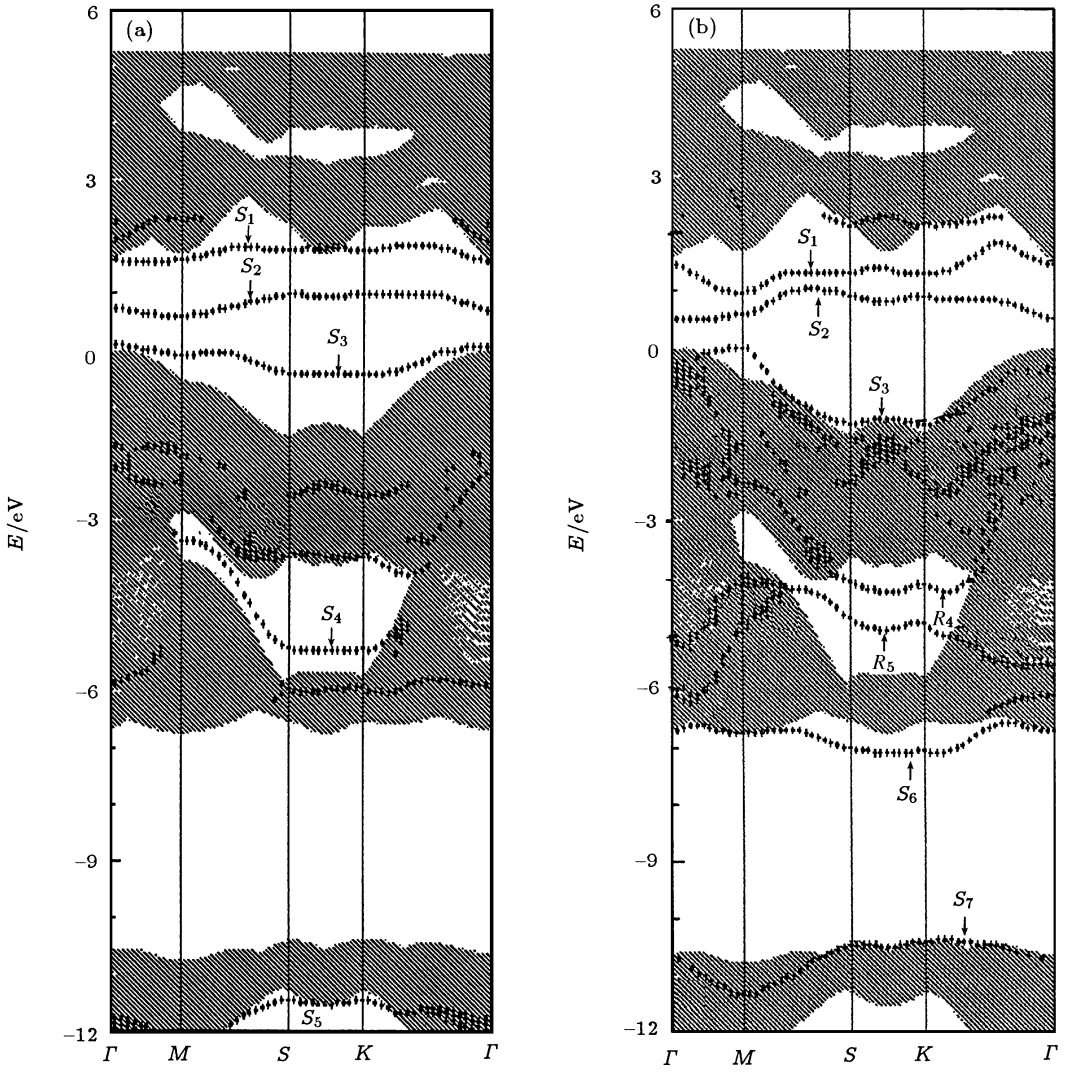


Fig.4. (a) Electronic structure in the bridge site model together with the projected bulk bands. (b) Electronic structure in the hollow site model together with the projected bulk bands.

In Figs.4(a) and 4(b), we show the surface band structure of the bridge site and the hollow site models, respectively. In contrast to the ideal bulk-terminated surface, the changes of the surface electronic states are remarkable. For the bridge site model (see Figs.3 and 4(a)), we immediately find no new surface state, and the differences between the surface properties are mainly reflected by the three surface states in the fundamental gap. The two topmost surface states move upwards by 0.1 and 0.4eV, respectively, and the lower surface state moves downwards by 0.1eV. Examining the layer density of states at the special point in the SBZ, we find that the occupation of the two topmost surface states becomes smaller and the occupation of the lower state becomes greater. Here we confine our attention to the hollow site model surface. By comparing with the ideal terminated case (see Figs.3 and 4(b)), we come to the following conclusions. (1) In the fundamental gap, the surface state S_1 moves upwards by 0.05–0.1eV, and the occupation of the density of states becomes smaller. The surface state S_2 moves upwards by 0.2–0.6eV, and the splitting of the surface

states S_1 and S_2 decreases by 0.5eV along the M–K line. Obviously, the surface state S_3 moves downwards very close to the bulk projected band along the Γ–K line; it goes into the bulk projected band and turns into a strong surface resonance state. It disperses heavily with a bandwidth of 1.0eV along the M–S and K–Γ lines. (2) In the stomach gap, the surface state S_4, corresponding to the ideal terminated surface, disappears and two new surface states occur. We denote these two surface states, R_1 and R_2. One surface state R_1 is located at about −4.0eV below the VBM and turns into a resonance state along the M–S and K–Γ lines. The other surface state, R_2, is located at about −5.0eV below the VBM and has a dispersion downwards by 0.9eV along the M–S line. The two surface states come from the p state of the Ga atom in the surface layer and the p state of the As atom in the sublayer. They correspond to the ppσ bond between the Ga–As atoms. (3) In the top of the heteropolar gap, along Γ–M–S–K–Γ, a new surface state occurs. It deviates from the projected bulk band by about 0.7eV at the S and K points. This surface state contains mainly the s state of the Ga atom in the surface layer and the s state of the Ga atom in the sublayer. It corresponds to the ssσ bond between the Ga–Ga atoms.

3.2. The surface band structure of the GaAs (311)B surface

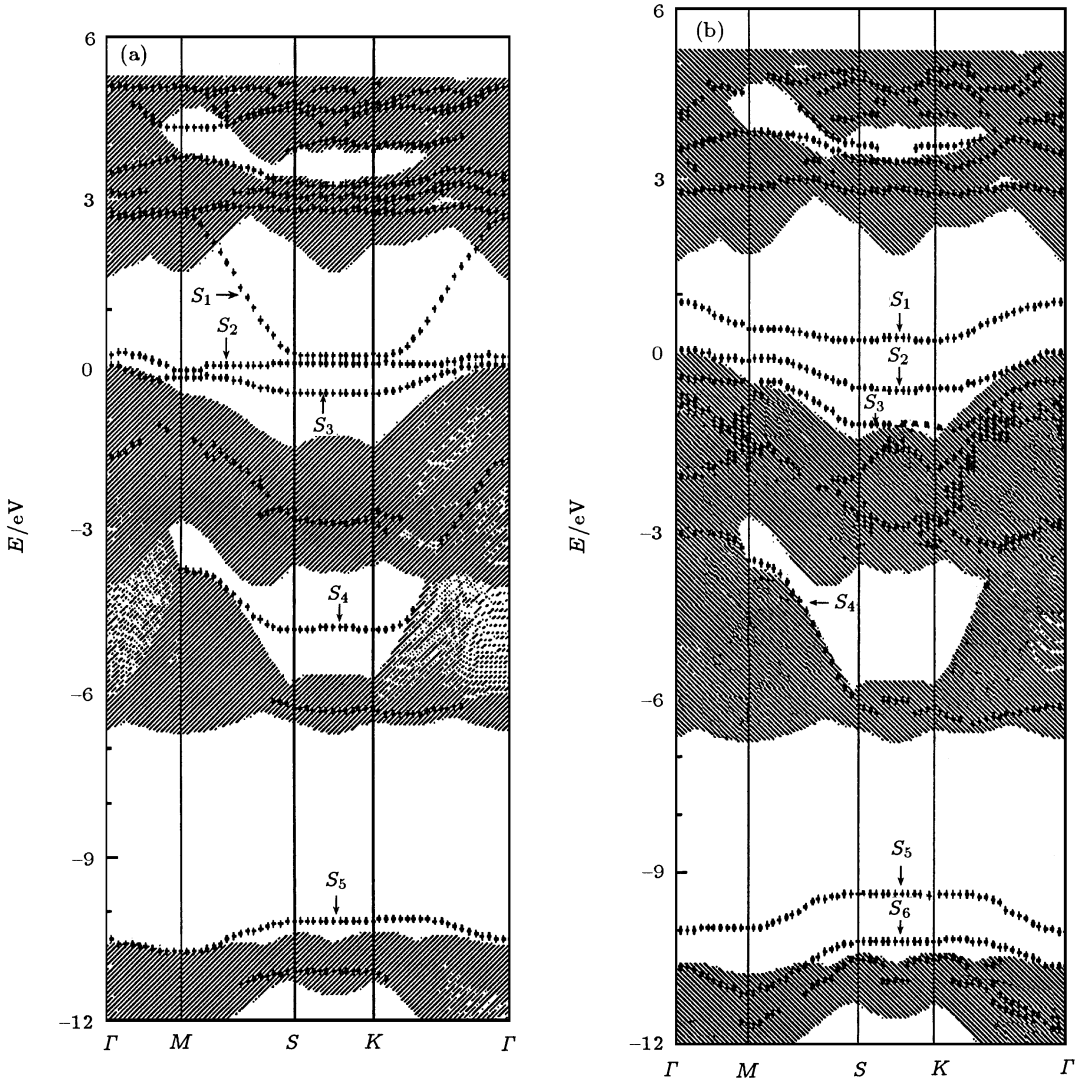


Fig.5. (a) Electronic structure of an ideal Ga-terminated GaAs(311)B (1×1) surface together with the projected bulk bands. (b) Electronic structure of an ideal As-terminated GaAs(311)B (1×1) surface together with the projected bulk bands.

In contrast to the (311)A surface, Figs.5(a) and 5(b) show the surface band structure of the Ga-terminated and the As-terminated (311)B surfaces, which correspond to the As-terminated and the Ga-terminated (311)A surfaces, respectively. Although the positions of the anions and the cations have now exchanged, we still find the same dangling bonds as for the (311)A surfaces. Since the atomic energy levels of the cations in the crystal are higher than those of the anions, the surface states will shift accordingly. This is confirmed by Fig.5. In Fig.5(a), the surface dangling-bond state of the cation, S_1, moves upwards at point Γ and disperses downwards heavily. The surface state S_2, the dangling-bond state of anions, moves downwards by 0.6eV. In the stomach gap, the surface state S_4, connected to the s state of the cation, moves upwards by 0.2eV. In the anion s-state-dominated area below the heteropolar gap, the surface state S_5 moves downwards by 1eV. By analysing Fig.5(b), the same conclusion can be obtained. It is interesting to note that there are two surface states below the heteropolar gap in Fig.5(b): the higher state stems from the As atoms in the top layer while the lower state originates from the As atoms in the sublayer.

4. Comparison with the ARUPS experiments

Two investigations by ARUPS of surface electronic states of the GaAs(311) surface have been reported recently.[15,17] In this section, we make a preliminary comparison of our theoretical results with the experiments. We focus on the comparison of the hollow site model with experiments. In the energy range of 7.0eV below the VBM, the authors identified six surface states along the Γ–K–M line (see Fig.3 in Ref.[15] and Fig.7 in Ref.[17]). From Fig.4(b), we have identified a total of eight surface states in this range. The difference between our calculation and the experiments is mainly that, in our calculation, there are two surface states in the fundamental gap. We think that the two top surface states, S_1 and S_2, obtained in our calculation can be tentatively assigned to two unoccupied surface states. Two surface states S_3 and R_1, at about -1.0 and -4.0eV, respectively, are confirmed by the experiments,[15,17] e.g. the surface state S_3 has a dispersion with a bandwidth of 0.9eV, which is in good agreement with the experimental value of 0.8eV. In our calculation, the surface state R_2 at about -5eV in the stomach gap is also identified by Olsson *et al.*[15] However, this state has not been observed in Ref.[17]. It should be pointed out that there is a new surface state S_6, localized at the upper heteropolar gap, derived from the ssσ bond of Ga–Ga atoms between the surface layer and sublayer. Although this surface state was observed in experiments, it was assigned to the bulk states.

Comparing the results of the bridge site model with those obtained in the experiments, we find that the difference is remarkable. Neither the number of the surface states nor the energy levels of these surface states are in agreement with the ARUPS measurement. So we conclude that the surface electronic states of the hollow site model are in agreement with the results of the ARUPS measurements, but those of the bridge site model are not. Therefore, the hollow site model is favourable for the Ga-terminated GaAs(311)A (1×1) surface, and the bridge site model should be excluded.

5. Summary

We have calculated the electronic states of high-index GaAs(311)A and GaAs(311)B surfaces by using the tight-binding method. The surface band structure together with the projected bulk band of both Ga-terminated and As-terminated surface layers for GaAs(311)A and GaAs(311)B are presented. In each case, the numbers of the surface states are determined, the localized surface features and orbital properties of these surface states along the Γ–Y–S–X–Γ high symmetry lines of the SBZ are discussed. For the Ga-terminated GaAs(311)A (1×1) surface, we have tested two possible structure models, the "bridge site " and the "hollow site" models. By comparing with the experimental results, we conclude that the hollow site model is favourable for the Ga-terminated GaAs(311)A (1×1) surface and the bridge site model should be excluded. These results will be useful for further study of the electronic properties of the GaAs(311) surface, both theoretically and experimentally.

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