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Electronic properties of sulfur-treated GaAs(001) surfaces

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We have studied the atomic geometries of the GaAs(001) As-terminated surfaces covered with sulfur overlayers by performing total-energy calculations within an empirical tight-binding model. A number of possible geometries are examined, and several geometries with low total energy are found to be free of surface states in the midgap. The surface band structures and local density of states for some of these geometries are calculated and the surface states are identified. Our results show that by forming a 2×1 reconstruction of sulfur overlayers in several different ways, good electronic properties of the GaAs surfaces can be obtained. This lends theoretical support to recent experimental studies in which the GaAs surface was treated with sulfur-related solutions.

I. INTRODUCTION

It is well known that untreated GaAs surfaces have poor electronic properties due to the formation of oxides on the surface. The oxidized surface typically contains many unsaturated bonds which result in a large density of surface states with energies near the middle of the bulk band gap. In the past there has been a considerable effort to improve the electronic properties of such surfaces, but with limited success. Recently, it has been demonstrated that a simple chemical treatment of the GaAs surfaces with sulfur-related solutions can lead to dramatic improvement of the electronic properties of the surface.[1-3] For example, a single passivation step of sulfide treatment can increase the current gain of a transistor from 30 to 2000,[1] a sulfide film deposited on GaAs epilayers at room temperature can increase the photoluminescence intensity by a factor of 2800 relative to the untreated ones,[2] and an $Al_xGa_{2-x}As$/GaAs heterostructure bipolar transistor can have near-ideal transport characteristics after such a treatment.[3] Within the last year, a great deal of experimental studies on the passivation of GaAs surfaces have been reported.[4-12] The results of these studies provide strong evidence that the sulfur termination of the GaAs surface is crucial in obtaining good electronic properties by dramatically reducing the number of electronically active surface states. These facts call for a detailed theoretical study of the atomic geometry as well as the electronic properties of (001) GaAs surfaces covered with sulfur overlayers.

We performed theoretical calculations on the As-terminated GaAs(001) surface covered with sulfur overlayers for a number of possible atomic geometries. We calculated their electronic structures and total energies by using an empirical tight-binding model with five orbitals (sp^3s^*) per atom.[13] For each possible geometry, the atoms on the top two layers of the surface are relaxed and their most stable positions are determined by minimizing their total energies. Then, the surface band structures and the local density of states for these geometries are calculated, and the origins of surface states are identified. Our results indicate that by forming a 2×1 reconstruction with every pair of surface As atoms bridged by either a sulfur atom or a disulfur molecule, or substituting one of the two As atoms which form the As dimer at the surface by a sulfur atom, desired electronic properties can be obtained, namely no surface states near the midgap. Our theoretical studies lend support to the experimental findings for sulfur-treated (001) GaAs surfaces.

This paper is organized as follows. In Sec. II we give a brief review of the total-energy calculation within an empirical tight-binding model and its application to surface problems. In Sec. III this procedure is applied to identify the stable atomic geometries of As-terminated GaAs(001) surfaces covered with sulfur overlayers. In Sec. IV we present surface band structures and local densities of states of several favorable (2×1) geometries. Section V concludes the paper with a discussion.

II. THE TOTAL-ENERGY APPROACH

The total energy E_{tot} of an electron-ion system can be expressed as

$$E_{\text{tot}}=E_{e\text{-}e}+E_{e\text{-}i}+E_{i\text{-}i}\ , \tag{1}$$

where $E_{e\text{-}e}$, $E_{e\text{-}i}$, and $E_{i\text{-}i}$ denote the electron-electron, electron-ion, and ion-ion interaction energies. In a one-electron band theory, one can calculate the sum of one-particle energies up to the Fermi level, denoted E_{BS},

$$E_{\text{BS}}=2\sum_{n,\mathbf{k}}E_n(\mathbf{k})\ , \tag{2}$$

where the sum is over occupied single-particle states with wave vector $\mathbf{k}$ and band index n. The factor 2 takes into account the spin degeneracy. E_{BS} is related to the electron-ion and electron-electron interactions by

$$E_{\text{BS}}=E_{e\text{-}i}+2E_{e\text{-}e}\ . \tag{3}$$

Note that electron-electron interaction in E_{BS} is counted twice.

The difference of the total energy, E_{tot}, and the band-structure energy, E_{BS}, is defined as U, and we have

$$U \equiv E_{i\text{-}i} - E_{e\text{-}e} \ . \tag{4}$$

As it is not possible to calculate U within the empirical tight-binding model, we resort to an approximation scheme due to Chadi.[14–16] This approach was used in the past to determine the atomic geometries of several III-V compound and group-IV elemental semiconductor surfaces with considerable success.[14–18] In this scheme, U is written as the sum of contributions from individual bonds,

$$U = \sum_i \Delta U(d_i) \ , \tag{5}$$

where d_i denotes the bond length of bond i. It is further assumed that the Taylor expansion of $\Delta U(d)$ can be truncated at second order:[14–16]

$$\Delta U(d) = U_0 + U_1[(d - d_0)/d_0] + U_2[(d - d_0)/d_0]^2 \ , \tag{6}$$

where d_0 is the equilibrium bond length for the bulk material. The coefficients U_0 and U_2 are related to the experimental values for the cohesive energy and the bulk modulus. Since the total energy for the bulk crystal should be a minimum at d_0, U_1 should exactly cancel the derivative of E_{BS} with respect to d at d_0.

The coefficients U_1 and U_2 for a number of bulk semiconductors determined within the sp^3s^* nearest-neighbor tight-binding model[13] are listed in Table I, together with the bond length and bulk modulus[19] used in the determination. Here a $1/d^2$ dependence[20] for the nearest-neighbor interaction parameters is assumed in the calculation of the derivative of E_{BS} with respect to d. In performing the summation over **k** in (2), we have chosen appropriate sets of special points for the bulk[21] and for the surface.[22]

The coefficient U_0 is independent of the relaxation of atoms in the system, but is important here since we wish to compare the total energies of systems with different number of chemical bonds. For later use, we calculated U_0 of the S—S and As—S bonds.

To calculate U_0, we use the following relation:

$$E_{\text{BS}} + U + E_{\text{coh}} = E_{\text{free}} \ , \tag{7}$$

where E_{BS} is defined in (2), the sum of one-particle band-structure energies of the crystal system, U is defined by (5) and (6), E_{free} is the total energy of all free atoms which form the crystal, and E_{coh} is the total cohesive energy.

We use the simplified slab model of Ref. 23 to calculate E_{BS} of As_2S_3, and use the ring coordinates of Ref. 24 to calculate the molecular energy of S_8. In these calculations we take the on-site energies of As in As_2S_3 as the on-site energies of As in GaAs, and determine the on-site energies of S by their differences in atomic-orbital energies from those of As.[23] The nearest-neighbor interaction parameters are taken as those of GaAs scaled be $1/d^2$. The cohesive energy of sulfur is taken as 2.85 eV/bond,[25] and the cohesive energy of the As—S bond is estimated as 2.93 eV/bond. When we estimate the cohesive energy of the As—S bond, we assume that the difference of the cohesive energies between the As—S and As—As bonds is the same as the difference of the bond strengths of their diatomic molecules.[26] In this way, the U_0 of the As—S bond is calculated as 6.31 eV/bond, and the U_0 of the S—S bond is calculated as 9.04 eV/bond. To be sure that our results make sense, we also calculated the S—S bond energy by using a diatomic model and its bond strength.[26] The calculated U_0 of S—S bond is 9.43 eV/bond, which is quite close to that calculated from the ring structure. We also calculated U_0 of the S—As bond in As_2S_3 by using the parameters given in Ref. 24, and the difference from the previous calculation is less than 0.5 eV. So, later on, when we compare the total energy of different surface structures, we took U_0 of the surface S—S and As—S bonds to be 9.04 and 6.31 eV/bond, respectively, which are calculated by using the same parameters as in the surface calculations. For comparison, we also calculated U_0 of bulk Si and Ge in the sp^3s^* model. The results are 5.85 and 5.41 eV/bond, respectively.

We calculated U_1 and U_2 of the As—As and As—S bonds at the surface, which are needed when we consider the change of the bond length. The tight-binding parameters of the As—As bond are taken from Larsen *et al.*,[27] and the bulk modulus is taken to be the same as for bulk GaAs. The relative change in bond length of As_2S_3 under pressure along an in-plane direction[28] is used to determine U_1 and U_2 of the As—S bond at the surface.

To calculate ΔU at the surface, we need to know the value of d_0 in (6). We always take d_0 as the ideal bond length, which is defined as the sum of covalent radii of the two atoms connected by the bond. The covalent radii used for Ga, As, and S are 1.26, 1.19, and 1.02 Å, respectively.

III. GaAs-SURFACE CALCULATIONS

We first calculate the total energy of a 2×1 reconstruction of the (001) GaAs surface. This reconstruction is obtained by forming an As dimer along the $[1\bar{1}0]$ direction

TABLE I. U_1 and U_2 of some semiconductor bonds determined within the sp^3s^* nearest-neighbor tight-binding model, together with their bond length d_0 and bulk modulus B used in the determination.

	C	Si	Ge	GaP	GaAs	GaSb	InSb	ZnSe
U_1 (eV)	−51.60	−20.29	−18.86	−18.50	−17.74	−15.58	−13.13	−17.83
U_2 (eV)	114.80	61.65	57.44	64.41	55.13	51.15	46.10	49.41
d_0 (Å)	1.54	2.35	2.45	2.36	2.45	2.64	2.81	2.45
B (10^{12} ergs/cm^3)	4.42	0.988	0.750	1.127	0.747	0.561	0.456	0.595

from an ideal As-terminated (001) GaAs surface within each 2×1 unit cell. We will take the total energy of this surface as a reference level for describing the total energies for sulfur-treated GaAs surfaces. By eliminating one out every four rows of dimers in the 2×1 reconstructed surface, one obtains a 2×4 reconstruction which is believed to be the most stable surface geometry for the As-terminated (001) GaAs surface in vacuum.[27] Based on simple electron-counting arguments, one can show that the 2×1 reconstruction would cause a charge-imbalance problem, whereas the 2×4 reconstruction would not. In each Ga—As bond $\frac{3}{4}$ electrons come from the Ga atom and $\frac{5}{4}$ electrons come from the As atom. In the 2×1 reconstructed surface, each As atom contributes $\frac{5}{2}$ electrons to the two backbonds, gives one electron to the As dimer bond, and leaves $\frac{3}{2}$ electrons for the lone pair. Thus, each 2×1 cell is one electron deficient. Since the lone-pair surface states lie below the Fermi level, electrons will flow from inside the semi-infinite slab to the surface, giving rise to a charged surface. By eliminating one out every four rows of dimers to form the 2×4 reconstruction, we create four Ga dangling bonds in each 2×4 unit cell. It can be shown that the energies of Ga dangling-bond surface states are higher than the Fermi level. Thus, the three excess electrons ($\frac{3}{4}$ from each dangling bond) can replenish the lone-pair states of the remaining three As dimers in the unit cell, and provide charge balance for the 2×4 reconstruction.

We perform calculations for a slab which consists of five (2×1) diatomic layers of GaAs normal to the [001] direction with one surface terminated by Ga atoms and the other by As atoms. A hydrogen atom is attached to each Ga atom at the Ga surface to passivate one Ga dangling bond, leaving the other dangling bond unoccupied. By doing this, we artificially get one excess electron per 2×1 cell from the Ga surface and use that electron to completely fill the lone-pair surface states of the dimerized As surface. Thus, our calculation for As dimers in the 2×1 reconstruction closely resembles that for As dimers in the 2×4 reconstruction, in which all As lone-pair states are completely filled. At the As surface, As dimers are formed along the [110] direction. Every As atom at the surface is threefold bonded with one dangling bond fully occupied (lone pair). The atomic positions of the surface As atoms are allowed to relax to minimize the total energy.

Our calculations show that when the total energy is minimized, As dimer atoms will relax *outward* (about 0.09 Å) from the ideal As dimer positions. The ideal dimer positions are defined such that the bond lengths between any two neighboring surface atoms are the sum of their covalent radii. For comparison, we also calculated the Ga-terminated surface with Ga-Ga dimers, which showed an *inward* (about 0.11 Å) relaxation from the ideal dimer positions. This result is in qualitative agreement with those of the first-principles calculations performed by Qian *et al.*[29,30] We found that the calculated total energy of the 2×1 GaAs surface with an As dimer is lower than that for the ideal GaAs surface by 4.25 eV $-U_0$ (As—As bond) per 2×1 unit cell. Since the result predicted by the first-principles calculation is 0.7 eV,[30] the U_0 per As—As bond at this surface is estimated to be 3.55 eV/bond.

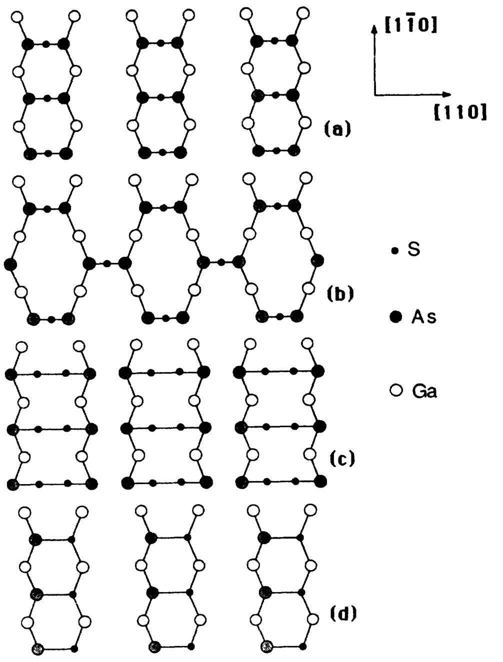

FIG. 1. Top view of four 2×1 geometries of GaAs(001) surfaces treated with sulfur-related solutions.

We then perform total-energy calculations for a series of possible geometries for GaAs(001) As-terminated surfaces covered with a sulfur overlayer. We first considered the simplest 1×1 geometry, with one sulfur atom per unit cell on the top layer (occupying a Ga site) bonded to two As atoms on the second layer. We have also considered another 1×1 geometry with each sulfur atom in the above replaced by a sulfur dimer, which is allowed to rotate about an axis normal to the surface to minimize the total energy. It is found that both of these surface geometries give rise to surface states in the midgap which are partially filled. Since these 1×1 surface geometries are unfavorable, we proceed to examine the possible 2×1 reconstructions.

We first examined three different 2×1 geometries as shown in Figs. 1(a)–1(c). For each geometry, we allow atoms on the first two layers to relax, and choose the one with the lowest total energy as the final stable structure. In Figs. 1(a) and 1(c) the surface has a 2×1 unit cell with two As surface atoms in the cell bridged by either a sulfur atom or a sulfur dimer. In Fig. 1(b) the surface has a $c(2\times2)$ unit cell which has similar a local-bonding configuration to Fig. 1(a). In this structure chain character is shown by the As—S bond and by the As—Ga bond in the next layer, which is very similar to the layered structure of As_2S_3.[23] For clarity, the side view of each unit cell in Figs. 1(a)–1(c) are shown in Fig. 2, where Fig. 2(a) corresponds to the unit cell of Figs. 1(a) and 1(b), and Fig. 2(b) corresponds to the unit cell of Fig. 1(c). All these geometries will have the charge-imbalance problem similar to that for the As dimer surface, i.e., each 2×1 unit cell is one electron deficient. This problem can be

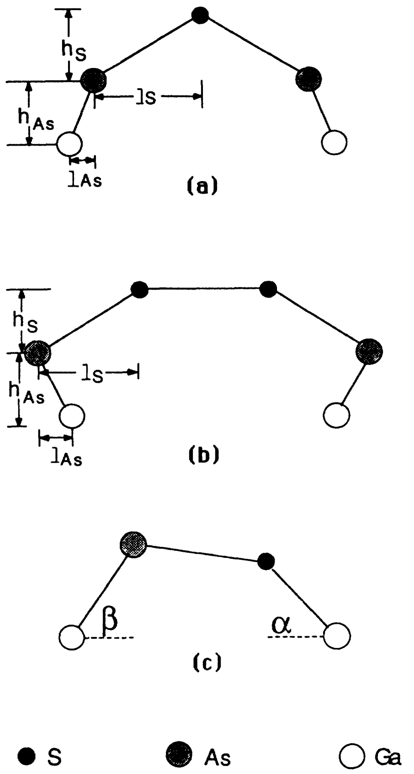

FIG. 2. Side view of geometries in Fig. 1, where (a) corresponds to Fig. 1(a) and 1(b), (b) corresponds to Fig. 1(c), and (c) corresponds to Fig. 1(d).

remedied, for example, by removing one As—S—As (As—S—S—As) unit in every four As—S—As (As—S—S—As) units to form a 2×4 reconstruction. Here, we study only the 2×1 reconstructed surfaces, and we artificially fill the lone-pair surface states by taking electrons from the other end of the slab, similar to what we have done for the As dimer surface. We expect the results for electronic structures obtained this way to resemble those for the more realistic 2×4 reconstructed surfaces.

We again perform calculations for a slab which consists of five (2×1) diatomic layers of GaAs normal to the [001] direction with one surface terminated by Ga atoms and the other by As atoms. A hydrogen atom is attached to each Ga atom at the Ga surface to passivate one Ga dangling bond, leaving the other dangling bond unoccupied, and a sulfur atom (or molecule) bridges the two As atoms within the unit cell at the As surface. In calculations of the first geometry and the reference surface with an As dimer, our results indicate that the bond-length changes in such relaxations are very small (less than 1%) when compared to the bond-angle changes. So, in the calculations for other surfaces, we keep the bond lengths the same as their ideal lengths and only consider the relaxations of bond angles.

We vary the vertical distance between the top sulfur layer and the next As layer, h_S, until the total energy for the surface is minimized. A schematic sketch which defines h_S is given in Fig. 2 and numerical values of h_S at which the total energy is minimized for geometries shown in Figs. 1(a)–1(c) are listed in Table II.

In Table II we also include the total energies of five geometries, i.e., the ideal As-terminated (001) surface, the As dimer 2×1 reconstruction, and the three geometries shown in Figs. 1(a)–1(c). All these total energies are measured with respect to the As dimer 2×1 reconstruction. The total energy of one or two free sulfur atoms (-28.9 eV/atom in our model) are subtracted when there is one or two sulfur atoms in each unit cell. The constant energy U_0 for the S—As and S—S bonds are included in the calculations. These results show that the ideal surface has the highest total energy, and the three geometries Figs. 1(a)–1(c) have similar total energies, which are substantially lower than the As dimer 2×1 reconstruction.

There is another possible 2×1 reconstruction which does not have the charge-imbalance problem. In this surface geometry one of the two As atoms in the As 2×1 surface is replaced by a sulfur atom [see Fig. 1(d)]. Based on the electron-counting argument given above, each surface As atom needs 0.5 electron to completely fill the lone-pair state. Since the sulfur atom has one more electron than the As atom, the substitution of one As atom by a S atom will lead to 0.5 excess electron, which exactly compensates for the other As atom in the unit cell. It is therefore interesting to examine the total energy and electronic structures of this reconstruction.

To calculate the total energy of this reconstruction, we again use a slab consisting of five GaAs diatomic layers. However, we do not need to pull electrons from one end of the slab to the other, since there is no charge imbalance in the present case. Thus, instead of attaching one hydrogen atom to each Ga atom on the Ga-terminated side of the slab, we add one more hydrogen atom to one of the two Ga atoms in the 2×1 unit cell. Namely, in each 2×1 unit cell one Ga atom is bonded to a hydrogen atom, and the other is bonded to two hydrogen atoms. In this way, charge will be balanced on both sides of the

TABLE II. Structure parameter h_S (see Fig. 2) and the total energy E_{tot} per (2×1) unit cell for five geometries of GaAs(100) surfaces. The five geometries are the ideal As-terminated surface, the 2×1 reconstruction with an As dimer, and the three geometries shown in Figs. 1(a)–1(c). The energy reference level is the total energy per unit cell of As dimer reconstruction, the second geometry here.

	Ideal As surface	(2×1) As dimer	Fig. 1(a)	Fig. 1(b)	Fig. 1(c)
h_S (Å)			0.965	1.062	1.697
E_{tot} (eV)	0.70	0	-6.09	-6.00	-7.69

slab. To find the equilibrium atomic positions for this reconstruction, we fix the bond lengths and allow the surface As and S atoms to relax by changing the bond angles until the total energy reaches a minimum. Since the S atom plays the role of an As atom here, we take the nearest-neighbor parameters for S—As and S—Ga bonds to be those for As—As (Ref. 27) and Ga—As bonds, respectively, scaled by $1/d^2$. Our results show that in equilibrium the angle between the S—Ga bond and the second-layer Ga plane (α) is approximately 48.5° and the angle between the surface As—Ga bond and the second-layer Ga plane (β) is approximately 61.0° [see Fig. 2(c)]. For comparison, in the reference As dimer surface the angle between the surface As—Ga bond and the second-layer Ga plane is approximately 55.0°.

However, it is not meaningful to compare the total energy of this structure with the 2×1 As dimer reconstruction, as we did for the previous three 2×1 geometries shown in Figs. 1(a)–1(c). The present 2×1 surface is charge neutral, whereas the As dimer surface is not. A more meaningful comparison would be between this surface and the As 2×4 reconstruction. This would require much larger computational effort, and we shall leave it for future investigations. Here we simply assume that the surface is more stable than the As 2×4 reconstruction and proceed to calculate its surface band structures.

IV. SURFACE STATES OF FOUR STABLE (2×1) GEOMETRIES

As mentioned above, by performing the total-energy-minimization calculations, we found four possible (2×1) geometries of As-terminated GaAs(001) surfaces covered with sulfur overlayers as shown in Figs. 1(a)–1(d). The surface band structures and local density of states of these surfaces are presented below.

The surface Brillouin zones for the above geometries are shown in Fig. 3, where large squares correspond to the surface Brillouin zone of GaAs with a 1×1 unit cell. The shaded area in Fig. 3(a) corresponds to the Brillouin zone for 2×1 surfaces as shown in Figs. 1(a), 1(c), and 1(d). The shaded area in Fig. 3(b) corresponds to the Brillouin zone of the $c(2\times2)$ surface shown in Fig. 1(b). We calculated the band structures of above four geometries by using slabs of five diatomic layers of GaAs, with sulfur overlayers on As-terminated surfaces. The effects of Ga-terminated surfaces (bonded with hydrogen atoms) at the other end of the slab are eliminated by removing the Ga-related surface states in the resulting band structure. Calculations are performed along the directions shown in Fig. 3. Results are shown in Figs. 4–7. In all figures, we also plotted the bulk bands projected on the corresponding directions, shown as shaded areas. The origins of the surface states are identified. The results of the local density of states for two geometries, i.e., Figs. 1(a) and 1(c), are shown in Figs. 8 and 9. In these figures, solid lines are for the surface sulfur layer and dashed lines are for the next As layer.

To identify the origin of surface states, we use density-of-states results and consider possible bonding and antibonding states associated with surface atoms. For example, in Fig. 1(a) each (2×1) unit cell has one sulfur atom, two As surface atoms, and then two Ga atoms, and so on. Each sulfur atom has six electrons and each As atom has five electrons. In this case, each (2×1) unit cell has altogether two sulfur lone pairs, two As lone pairs, two S—As bonding states, and two S—As antibonding states. Generally speaking, lone-pair states are weakly coupled, but the bonding and antibonding states involve strong coupling of atomic orbitals and are far separated in energy, with the bonding state occupied and the antibonding state empty. Combining this analysis with density-of-states results (Fig. 7), we have identified the surface states

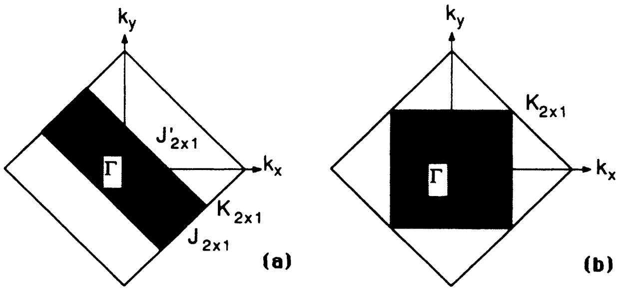

FIG. 3. Surface Brillouin zones for geometries in Fig. 1, where the large squares correspond to the surface Brillouin zone of the 1×1 structure, the shaded area in (a) corresponds to the surface with a 2×1 unit cell as in Figs. 1(a), 1(c), and 1(d), and the shaded area in (b) corresponds to the surface with a 2×1 unit cell as in Fig. 1(b).

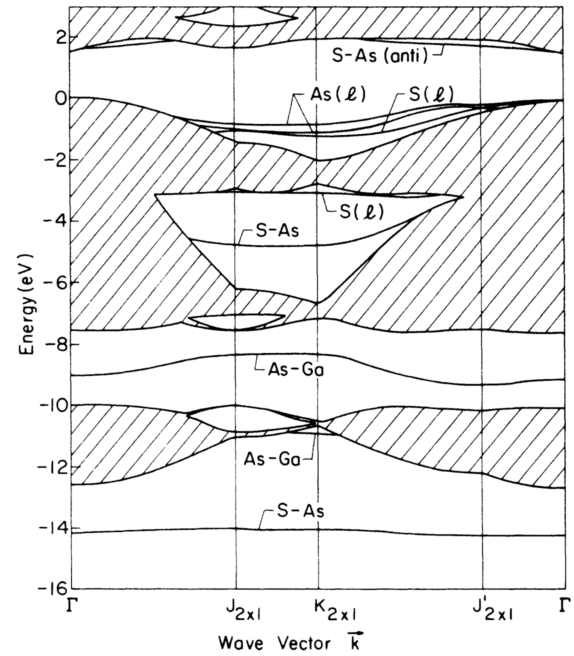

FIG. 4. Surface states of a sulfur-treated GaAs(001) surface with the geometry shown in Fig. 1(a) for wave vectors along symmetry directions shown in Fig. 3(a).

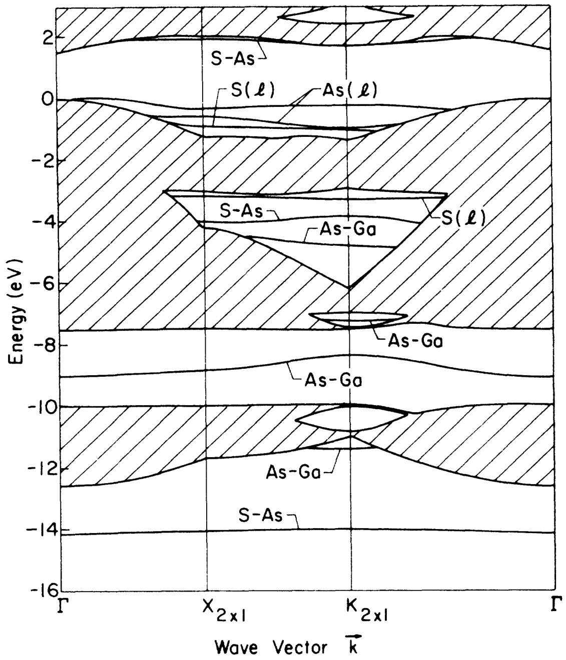

FIG. 5. Surface states of a sulfur-treated GaAs(001) surface with the geometry shown in Fig. 1(b) for wave vectors along symmetry directions shown in Fig. 3(b).

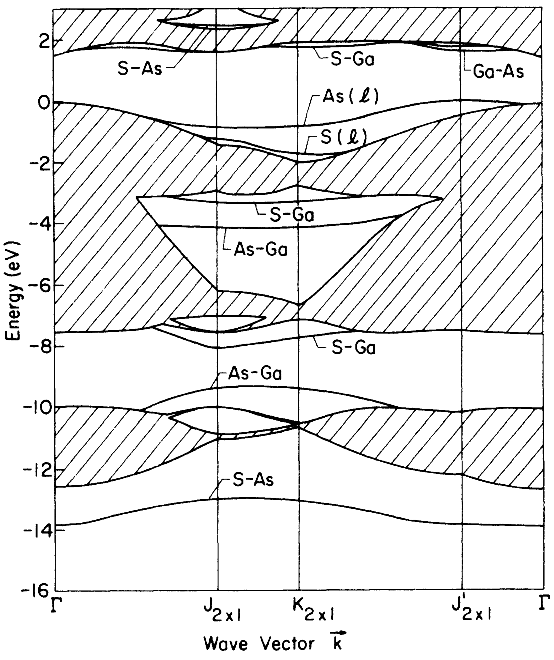

FIG. 7. Surface states of a sulfur-treated GaAs(001) surface with the substituted dimer as stated in Secs. III and IV for wave vectors along symmetry directions shown in Fig. 3(a).

as shown in Fig. 4. Similarly, in a disulfur-covered surface, Fig. 1(c), there is one bonding and one antibonding state between the two sulfur atoms. Comparing this to the previous case, the disulfur-covered surface has four more surface states, of which two are associated with the S—S bond (one bonding and one antibonding) and two are additional sulfur lone pairs. Using density-of-states results (Fig. 8), we have identified the surface states as shown in Fig. 6. These results are compared with x-ray-photoemission-spectroscopy (XPS) data of layered As_2S_3,[23] which contains As—S bonds, XPS data of a S_8 (Ref. 24) ring structure, which contains S—S bonds, and XPS data of GaAs(001) surfaces covered with sulfur overlayers, which show evidence of both As—S and S—S bonds.[5,7] Our results are consistent with these data.

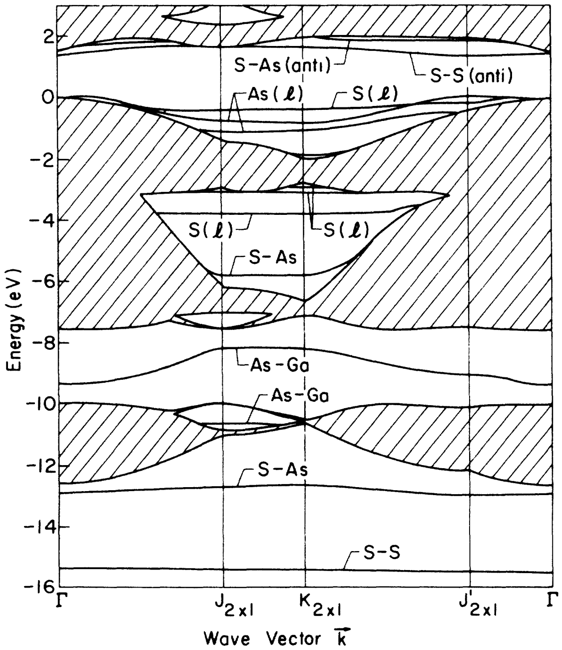

FIG. 6. Surface states of a sulfur-treated GaAs(001) surface with the geometry shown in Fig. 1(c) for wave vectors along symmetry directions shown in Fig. 3(a).

We have also studied the surface atomic positions and the surface band structures of GaAs(001) surfaces covered with a selenium overlayer with similar geometries. We found that the surface band structures of selenium-covered surfaces are similar to those of the sulfur-covered surfaces.

V. DISCUSSION

One common feature of the results in Figs. 4–7 is that they all have a band gap of at least 1.45 eV and are free of midgap surface states. This important feature explains the much improved electronic properties of a GaAs(001) surface covered with sulfur overlayers, and gives definitive correlation between the surface structures and their electronic properties. In Figs. 5–7 there are some surface states with energies very close to the top of valence band. These surface states could be moved below the top of the valence band with some small adjustment of the interaction parameters among the surface atoms. Given the uncertainty of the tight-binding model, these surface states can be viewed essentially as the same as

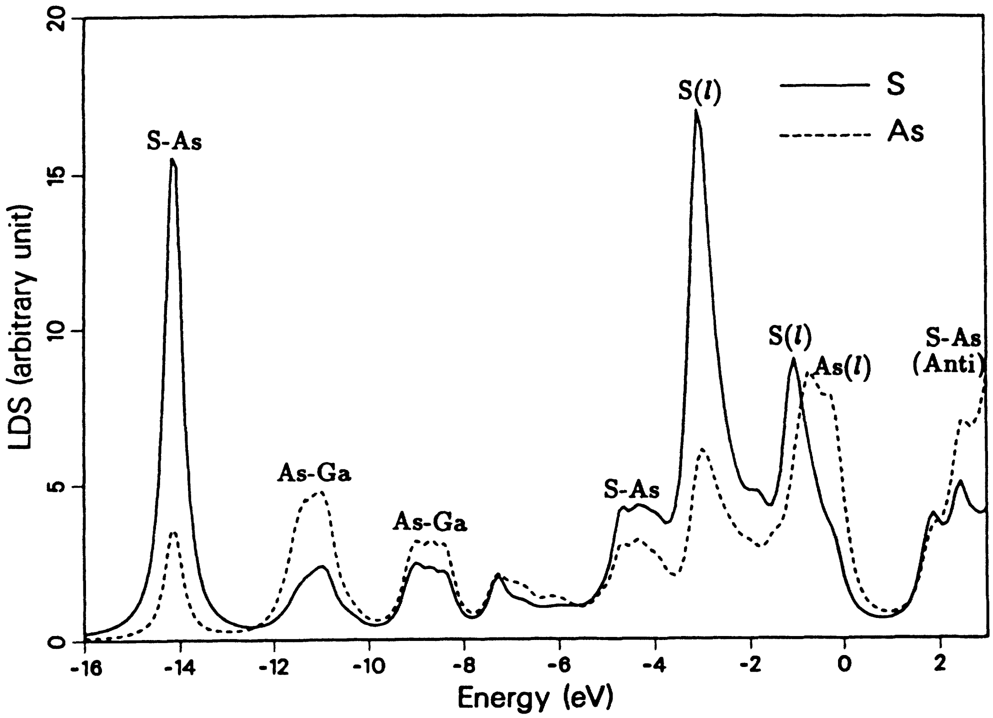

FIG. 8. Local density of states for geometry in Fig. 1(a). Here solid lines are results of surface sulfur layers and dashed lines are results of the next As layers. This figure corresponds to the surface states in Fig. 4.

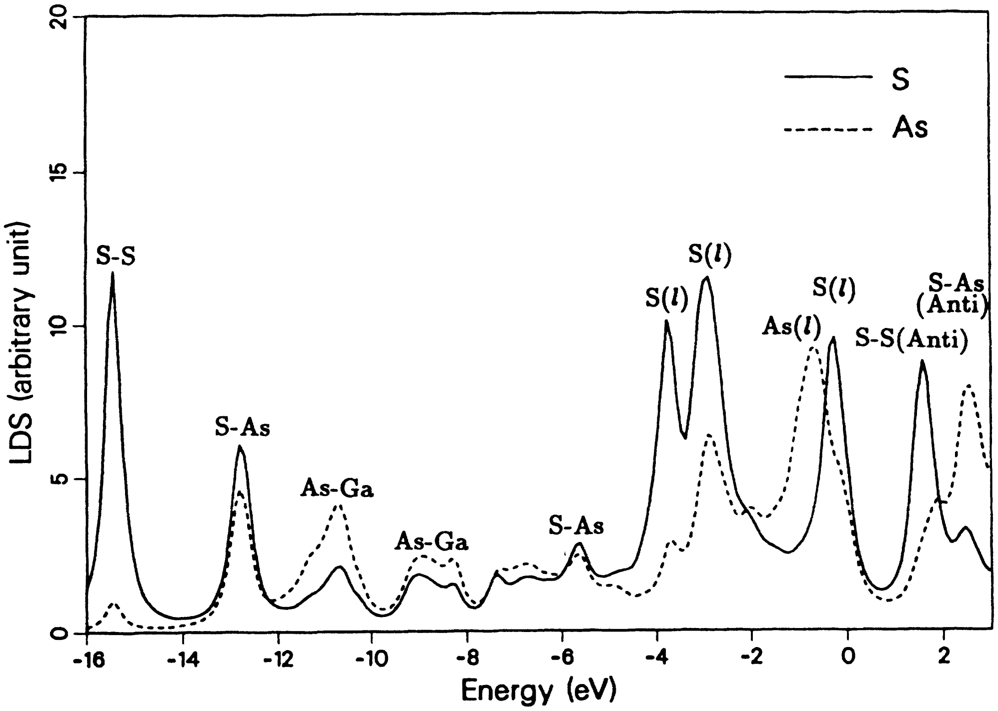

FIG. 9. Local density of states for geometry in Fig. 1(c). Here solid lines are results of surface sulfur layers, and dashed lines are results of the next As layers. This figure corresponds to the surface states in Fig. 6.

those inside, but near the top of, the valence band.

As we can see in Table II, the three structures of Figs. 1(a)–1(c) have a lower total energy than the As dimer reconstruction. We have difficulty in determining the total energy of the structure shown in Fig. 1(d) with respect to the As dimer reconstruction. It is possible that this structure may be more stable than the As 2×4 reconstruction. All these reconstructions are quite likely to form after chemical treatment by sulfur-related solutions. There is some evidence that the Ga—S bond exists for some sulfur-treated GaAs surfaces,[7] which may be explained by the formation of the structure shown in Fig. 1(d). The surface structure of the geometry in Fig. 1(c) is very similar to the layered structure of As_2S_3,[23] which is stable and has glass-forming properties. Sandroff *et al.* mentioned that in their experimental results the bonds between As and S atoms are strong, "even after a thorough water rinse roughly $\frac{1}{2}$ monolayer of sulfur could be detected on the surfaces."[1] Cowans *et al.* also obtained approximately 0.6 monolayer of sulfur.[11] It is possible that such a fraction of a monolayer of sulfur corresponds to combinations of the above four geometries. The calculated good electronic properties of these structures thus provide a theoretical explanation of the much improved measured electronic properties of the treated surfaces. These calculated results are consistent with the experimental observations, and they provide a better undertstanding of the aspects of S passivation of the As-terminated GaAs surfaces.

In summary, we have calculated the total energies and the electronic states of several GaAs(001) surfaces covered with sulfur overlayers. We found several 2×1 structures and a $c(2\times2)$ structure which have lower total energy than the As-terminated (2×1) surface and desirable electronic properties. These findings agree with the experimental observations. The real experimental situation is apparently much more complicated than the models considered here. For example, the sulfur overlayer could also be bonded to other chemical species such as oxygen (O) or hydroxyl (—OH), and the chemically treated surface is not necessarily an ordered surface, and it may have more complicated reconstructions. On the other hand, our calculations provide a profound connection between surface-electronic properties and local chemical bonding, and give a microscopic understanding of why these chemical treatments are so effective at reducing the GaAs surface states.

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[1] C. J. Sandroff, R. N. Nottenburg, J.-C. Bischoff, and R. Bhat, Appl. Phys. Lett. **51**, 33 (1987).

[2] B. J. Skromme, C. J. Sandroff, E. Yablonovich, and T. Gmitter, Appl. Phys. Lett. **51**, 2022 (1987).

[3] L. A. Farrow, C. J. Sandroff, and M. C. Tamargo, Appl. Phys. Lett. **51**, 1931 (1987).

[4] R. N. Nottenburg, C. J. Sandroff, D. A. Humphrey, T. H. Hollenbeck, and R. Bhat, Appl. Phys. Lett. **52**, 218 (1988).

[5] C. J. Sandroff, M. S. Hedge, L. A. Farrow, C. C. Chang, and J. P. Harbison, Appl. Phys. Lett. **54**, 362 (1989).

[6] C. J. Sandroff and M. S. Hegde (unpublished).

[7] C. J. Sandroff (private communication).

[8] C. J. Spindt, R. S. Besser, R. Cao, K. Miyano, C. R. Helms, and W. E. Spicer, Appl. Phys. Lett. **54**, 1148 (1989).

[9] H. H. Lee, R. J. Racicot, and S. H. Lee, Appl. Phys. Lett. **54**, 724 (1989).

[10] E. Yablonovitch, B. J. Skromme, R. Bhat, J. P. Harbison, and T. J. Gmitter, Appl. Phys. Lett. **54**, 555 (1989).

[11] B. A. Cowans, Z. Dardas, W. N. Delgass, M. S. Carpenter, and M. R. Melloch, Appl. Phys. Lett. **54**, 365 (1989).

[12] H. Hirayama, Y. Matsumoto, H. Oigawa, and Y. Nannichi, Appl. Phys. Lett. **54**, 2565 (1989).

[13] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[14] D. J. Chadi, Phys. Rev. B **19**, 2074 (1979).

[15] D. J. Chadi, Phys. Rev. B **29**, 785 (1984).

[16] D. J. Chadi, J. Vac. Sci. Technol. A **5**, 834 (1987).

[17] C. Mailhiot, C. B. Duke, and Chadi, Surf. Sci. **149**, 366 (1985).

[18] C. Mailhiot, C. B. Duke, and Chadi, Phys. Rev. B **31**, 2213 (1985).

[19] Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology,* edited by K. H. Hellwege (Springer, New York, 1982), Gp. III, Vols. 17a and 17b.

[20] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[21] D. J. Chadi and Marvin L. Cohen, Phys. Rev. B **8**, 5747 (1973).

[22] S. L. Cunningham, Phys. Rev. B **10**, 4988 (1974).

[23] S. G. Bishop and N. J. Shevchik, Phys. Rev. B **12**, 1567 (1975).

[24] W. R. Salaneck, N. O. Lipari, A. Paton, R. Zallen, and K. S. Liang, Phys. Rev. B **12**, 1493 (1975).

[25] C. Kittle, *Introduction to Solid State Physics,* 5th ed. (Wiley, New York, 1976), p. 74.

[26] *CRC Handbook of Chemistry and Physics,* 69th ed., edited by R. C. Weast (Chemical Rubber Co., Cleveland, 1988-1989).

[27] P. K. Larsen, J. F. van der Veen, A. Mazur, J. Ploomann, J. H. Neave, and B. A. Joyce, Phys. Rev. B **26**, 3222 (1982).

[28] Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology,* edited by K. H. Hellwege (Springer, New York, 1982), Gp. III, Vol. 17e.

[29] G.-X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. Lett. **60**, 1962 (1988).

[30] G.-X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1988).

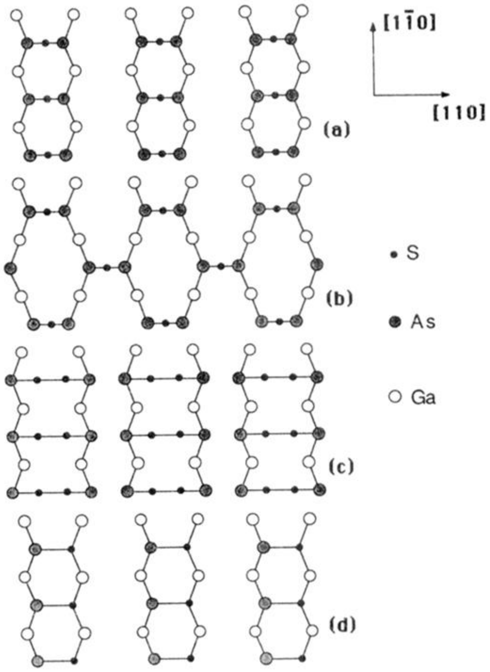

FIG. 1. Top view of four 2×1 geometries of GaAs(001) surfaces treated with sulfur-related solutions.

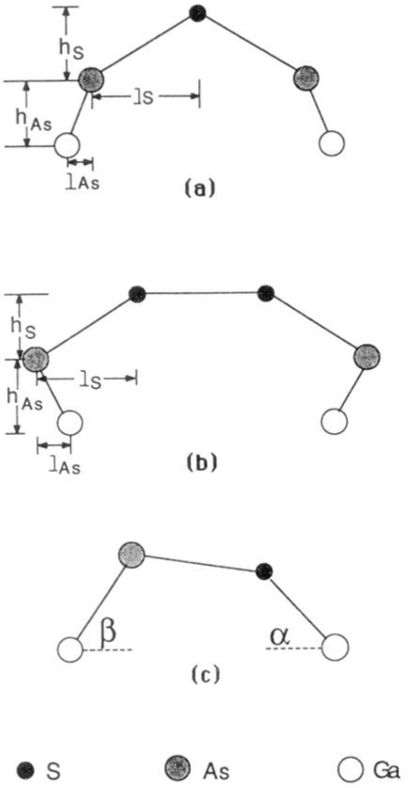

FIG. 2. Side view of geometries in Fig. 1, where (a) corresponds to Fig. 1(a) and 1(b), (b) corresponds to Fig. 1(c), and (c) corresponds to Fig. 1(d).

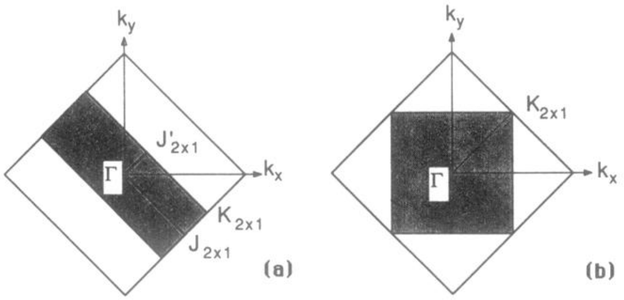

FIG. 3. Surface Brillouin zones for geometries in Fig. 1, where the large squares correspond to the surface Brillouin zone of the 1×1 structure, the shaded area in (a) corresponds to the surface with a 2×1 unit cell as in Figs. 1(a), 1(c), and 1(d), and the shaded area in (b) corresponds to the surface with a 2×1 unit cell as in Fig. 1(b).