First-principles pseudopotential calculations of passivated GaAs(001) surfaces

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An *ab initio* pseudopotential density-functional study of GaAs(001) surface passivated with sulfur is presented. A significant reduction of slab size is achieved by using hydrogen capping. Total energies and Hellmann-Feynman forces are calculated and used to guide the searches for stable structures. Results on sulfur monolayer coverage are in good agreement with other studies. Possible passivated 2×1 structure involving AsS or GaS dimers are investigated. The structural parameters are determined and the surface band characters are analyzed. The electronic structures show that some of the 2×1 structures studied have no surface states in the bulk gap and could be the important components of the passivated GaAs(001). [S0163-1829(96)09848-7]

One of the main obstacles that hinders the development of GaAs based devices is the poor surface electronic properties of GaAs surfaces. It is well known[1] that an untreated GaAs(001) surface has a high surface density of states that causes a high recombination rate and Fermi level pinning. To passivate this surface is to reduce the surface density of states at the Fermi level, or better yet, to remove the surface states from the bulk gap. The first successful passivation using Na_2S chemical treatment was reported in 1987.[2] Since then several other sulfur treatment methods have been developed.[3–6] There are a large number of reports on the improved electronic properties of passivated GaAs(001) surfaces in terms of enhanced photoluminescence and reduced band bending. However, the surface structure of the passivated GaAs(001) remains controversial. Some earlier studies considered the As–S bond to be the main feature,[7] while others have proposed that the surface is covered with S and As dimers.[8] Some studies have found that the passivated surfaces were As deficient,[9] and there were suggestions that the formation of the Ga–S bond was the key for passivation.[10] Structure of the passivated surface was assumed to be 1×1 with full sulfur coverage,[5] while several experiments[8,11] suggested that the structure responsible for the passivation was 2×1, possibly due to a dimerization of the S. Also, the sulfur coverage was found to depend on passivation procedures[12] and there were reports that some of the passivated surfaces had only half a monolayer of S.[12,13] Recent x-ray photoemission spectroscopy measurements on the core-level shifts[10,14] indicated that the sulfur was bonded to Ga, and the As–S bond signal disappeared after a simple cleansing of the passivated surfaces.

Several theoretical studies[15–18] have shown reduced surface density of states for various passivated structures. The complex structure of various passivated surface models makes first-principles calculations difficult to perform. The possible S dimerization was studied using the first-principles pseudopotential method,[16] and the energy of dimerization was found to be small. In addition, results[16] showed that the surface states were not removed from the bulk gap so the passivated surface remained metallic.

In discussions of surface electronic properties, a simple electron counting method is often invoked. This method concentrates on the number of electrons in the surface dangling bonds. Since each bond can be saturated with two electrons, an odd number of electrons in the surface unit cell will lead to a metallic surface while an even number will give an insulating surface. Using this electron counting method and based on their experimental results, recently Wang and Weinberg proposed[19] a model of passivated GaAs(001) that is consistent with a nonmetallic state (an even number of surface dangling bond electrons in the unit cell). In their model, the Ga terminated GaAs(001) is covered with a layer of either GaS or AsS dimers. The model has a 2×1 symmetry, which has been observed by several groups[8,11] on the sulfur treated GaAs(001) surfaces.

In this paper we report a first-principles pseudopotential study on the surface and electronic structures of several passivated GaAs(001) 2×1 structures. Both Ga and As terminated surfaces with either GaS or AsS dimer coverages are investigated. We have found that S binds strongly with Ga. But the Ga terminated (001) surface covered with a GaS dimer layer is still metallic. We have also found several structures that are nonmetallic. In particular, the AsS underlayer model appears to have many of the desired properties of the passivated GaAs(001).

In our study, the GaAs(001) surface is modeled by a slab consisting of three double layers of GaAs(001). Figure 1 shows the geometry of the slab. The slab is stacked along the [001] direction with a periodicity of 16.5 Å. One passivation layer is added to cover either the Ga or the As side of the slab. The other side is capped with hydrogen. The vacuum region between the slabs is about 8 Å thick. The theoretical equilibrium lattice constant of 5.50 Å is used for the unrelaxed substrate to avoid strains on the surfaces that may alter the equilibrium structures.

Total energy and electronic structure calculations are performed using the first-principles pseudopotential method,[20] which is based on the local-density approximation (LDA) of the density-functional theory.[21] The norm-conserving scheme[22] is used to generate pseudopotentials of Ga, As, and S. A total-charge exchange-correlation scheme[23] is used for Ga and As due to their large core sizes. Plane waves up to a kinetic energy of 7 Ry are used to expand the wave function. A mesh of 16 k-points in the full two-dimensional 1×1 Brillouin zone (BZ) is used in self-consistent calculations.

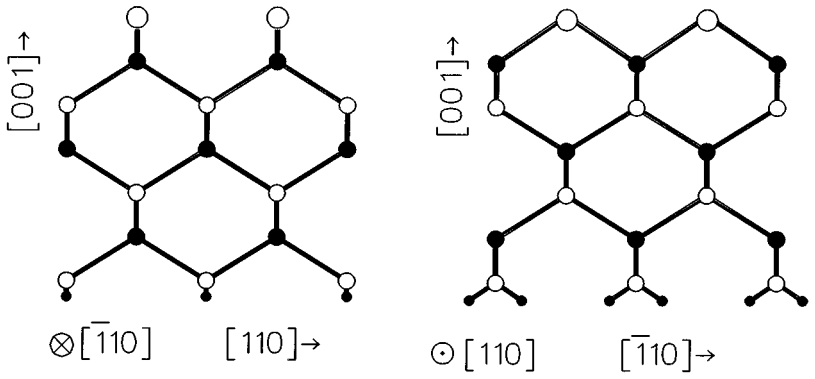

FIG. 1. Structure of passivated, Ga terminated GaAs(001). Filled and open circles denote Ga and As atoms, respectively. Hydrogen is denoted by small filled circles. The large open circle denotes passivation layers.

The geometry of the passivation layer is fully relaxed according to Hellmann-Feynman atomic forces.[24]

Because the GaAs(001) is a polar surface, there will be charge transfer between the two sides of the slab if both sides are left as free surfaces. To prevent this charge transfer, two fictitious hydrogen atoms of charge 0.75 (1.25) are used to cap the arsenic (gallium) dangling bonds. In order to determine the optimal hydrogen capping position, the plane-averaged potential of the slab is evaluated and compared with that of GaAs bulk along the [001] direction. Both the bond length and the bond angle of the capping hydrogens are adjusted to achieve the best agreement between these two potentials (see Fig. 2). We have found that for GaAs(001), both the bond length and bond angle need to be adjusted to obtain the best capping results. To cap the arsenic side, the best result is obtained with a bond length of 1.01 Å and a bond angle of 129.7°. To cap the gallium side, the bond length is 1.15 Å and bond angle is 116.2°. In comparison, the ideal tetrahedral bond angle is 109.5°. This hydrogen capping method was used in our earlier studies of GaAs(110)[25] with satisfactory results. It can be seen from Fig. 2 that even though the slab has only three double layers of GaAs, two of the double layers have bulklike potentials. The plane-averaged potential on the interior Ga layer is also used to align the slab electronic bands with the projected bulk bands.

The slab described above is asymmetric. This can cause an artificial electrostatic field in the vacuum region that may exert forces on the surface atoms and affect the surface structure. To compensate this artificial field, a dipole layer is placed at 2.5 Å above the hydrogen-capped side of the slab. The dipole moment is adjusted during the search of stable structures to maintain a zero electric field in the vacuum region. It can be seen from Fig. 2 that the dipole layer has no effect within the slab; only the vacuum region potential is affected. Although this procedure introduces one more parameter in the total energy minimization search, it allows calculations to be performed on a relatively thin slab. It is computationally much more efficient than using a double supercell[16] to restore the zero electric field in the vacuum region.

The equilibrium structures are determined by the minimum total energy and the minimum atomic forces on the passivation layer. We first studied a Ga terminated surface covered with a monolayer of S at the bridge site. The equilibrium S position is at 1.23 Å above the surface Ga, in good agreement with another calculation[16] and the x-ray standing-wave measurements.[26] We have also performed calculations without the dipole layer to balance the artificial field in the vacuum region, and found the equilibrium S height at 1.10 Å. This difference can be understood from Fig. 2. Without the dipole layer, the plane-averaged potential of the S covered surface shows an electric field pointing into the S covered side of the slab (notice that Fig. 2 shows the electronic potentials). The positive S core is therefore pushed to a lower height. This demonstrates that the artificial field caused by the asymmetry of slab has a small effect on surface structures.

To study the electronic structure of passivated GaAs(001), it is instructive to start from the ideal clean surface. Figure 3 shows the three highest occupied bands on the ideal As terminated surface. There are two dangling bonds per surface atom on the (001) surface. They form one π bond perpendicular to the surface and one σ bond parallel to the surface along the [110] direction (see Fig. 1). On the ideal 1×1 surface, the π bond forms a narrow surface band (labeled

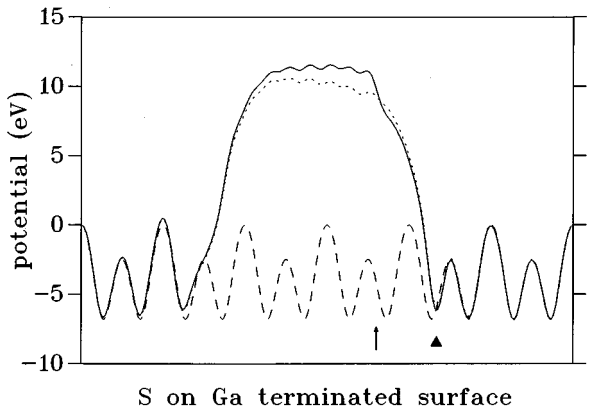

FIG. 2. Plane-averaged potentials for S covered Ga terminated 1×1 surface. Dashed line is the bulk value, the higher potential is the Ga plane. Dotted line is with hydrogen capping, the position of hydrogen is indicated by the triangle. The potential agrees with bulk on the capped side of the slab. Solid line is with hydrogen capping and a dipole layer, indicated by the arrow.

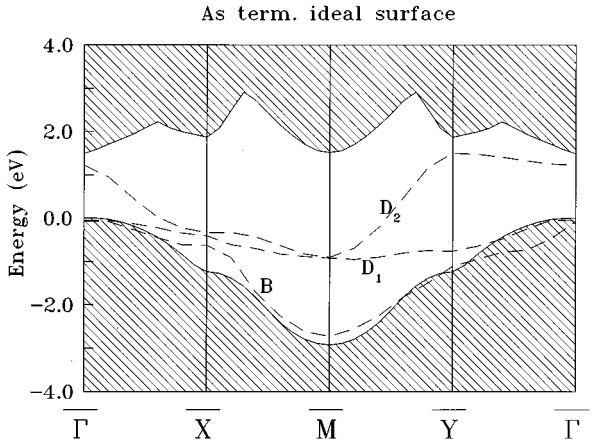

FIG. 3. Electronic structure of As terminated GaAs(001) ideal surface. The surface dangling bond is along the [110] direction (Γ-X direction). Shaded areas are bulk continuum.

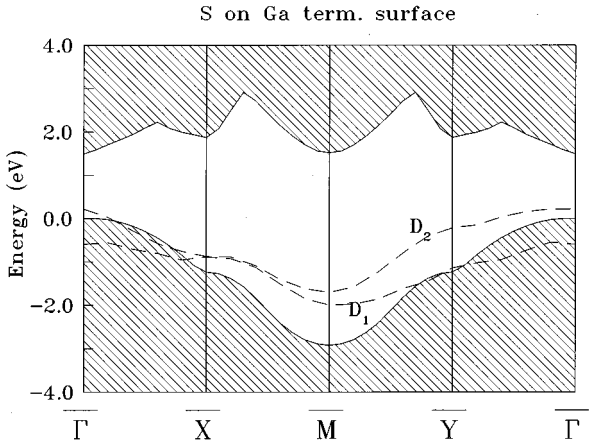

FIG. 4. Electronic structure of S covered, Ga terminated GaAs(001) 1×1 surface. The dangling bond of sulfur is along the Γ-X direction.

D_1 in Fig. 3) due to its small overlap with the neighboring π bond. The σ bond, on the other hand, with its significant overlap with the neighboring σ bond, forms a dispersive surface band D_2. The dispersion is particularly strong along the dangling bond direction (the Γ-X direction) and the dispersion perpendicular to the dangling bond is weak.

The band structure in Fig. 3 shows that besides the D_1 and D_2 bands discussed above, there is another band labeled B. This is almost a bulk band, since it is mostly within the bulk continuum and has almost symmetric dispersion along the X and Y directions. The wave-function density of this band reveals that it is the bonding state between the surface As and the sublayer Ga. The difference in energies at X and Y indicates that this band has some surface character, because for bulk bands the [110] and [$\bar{1}$10] directions are equivalent and energies at X and Y should be the same.

The As terminated surface has 2.5 electrons per surface atom occupying the surface bands, so the Fermi level is in the wide D_2 band. For the Ga terminated surface, there are only 1.5 electrons per surface atom to fill the surface bands. Therefore, the Fermi level falls into the narrow D_1 band, causing a higher surface density of states. Experimentally, surfaces grown in the As rich environment have shown better electronic properties.[8] However, As is chemically less stable than Ga on the surface, so most clean GaAs(001) surfaces are Ga rich.

One can simply replace the top layer As with S and obtain the S covered, Ga terminated surface. Figure 4 shows the band structure of such surface. The band B discussed above has been pushed into the bulk continuum, so there are only two surface bands inside the fundamental gap. Because of the strong attractive S potential, the surface bands are less dispersive than those of the ideal As terminated surface, particularly along the $\bar{M}$-$\bar{Y}$ direction. Now there are 3.5 electrons per surface atom in the two surface bands, so the Fermi level is near the top of D_2 band. The general feature of the band structure shown in Fig. 4 compares well with an earlier calculation.[16]

Under a 2×1 reconstruction, each of the surface bands folds into two subbands at half way of Γ-X as well as half way of $\bar{Y}$-$\bar{M}$. Possible S dimerization will split the two D_2 subbands, with the lower D_2 subband becoming the dimer bond. Dimerization also causes a mixture of D_1 and D_2 bands. A nonmetallic surface will appear if the Fermi level falls in one of the gaps between the surface bands. As discussed in the preceding paragraph, there are seven electrons in the surface bands of the 2×1 structure. Thus, the surface dangling bonds are not saturated. So S dimerization will not produce a nonmetallic surface. In addition, the x-ray standing-wave experiment[26] showed no sign of S dimerization.

A AsS dimer has one less electron than the S dimer. There are six electrons in the surface bands so it is possible for the Fermi level of the Ga terminated surface under AsS coverage to fall in a band gap. It is also possible for the same surface under GaS coverage to be nonmetallic. Similar counting shows that a GaS dimer layer on the As terminated surface, with six electrons in the surface bands, is another possible insulating surface.

The equilibrium surface structures of these three possibly insulating passivated surfaces are investigated using the total energy and atomic force calculations. All three structures have the observed 2×1 symmetry. Eight k-points in the full 2×1 BZ are used for self-consistent calculations. Atomic forces on the dimer layer are reduced to about 5 mRy/a.u. Relaxation of the second layer has not been investigated. Most of the forces on the second layer are less than 15 mRy/a.u., except for the Ga terminated surface under AsS coverage, where forces on the order of 30 mRy/a.u. are observed on the second layer. The structure parameters for these three surfaces are summarized in Table I. Sizable relaxations of the top layer atoms are found in all three cases. The main relaxation is along the [110] direction due to the formation of dimers. Also shown in Table I are the dimer bond lengths, which are around 2.6 Å.

The electronic structure is calculated with the optimized surface structure. A regular mesh of 72 k-points in the BZ are used to obtain the band gap and the surface valence band edge. For a Ga terminated surface under AsS dimer coverage, the surface conduction band is the upper D_2 subband. The lower D_2 subband drops well below the bulk band edge,

TABLE I. Structural parameters of passivated 2×1 surfaces. The distances are relative to the ideal positions, in units of Å.

	AsS Ga term.	GaS Ga term.	GaS As term.	AsS underlayer
S				
[001]	0.00	0.03	−0.17	−0.06
[110]	−0.66	−0.39	−0.62	
As or Ga				
[001]	0.05	−0.58	−0.03	−0.08
[110]	0.62	1.01	0.54	
dimer bond length	2.61	2.57	2.74	3.89

indicating the formation of a strong AsS dimer bond. Charge density shows that the dimer bond is polarized towards S, as one would expect. The splitting of the two D_1 subbands is mostly due to the different ionic potentials of S and As. The lower D_1 subband corresponds to the lone pair on S and is below the bulk band edge. The lone pair on As corresponds to the upper D_1 subband (labeled D_1 in Fig. 5), which is quite dispersionless. Band B in Fig. 5 is the back-bonding band of the AsS dimer with the substrate Ga, similar to the case of the ideal As terminated surface discussed earlier. As shown in Fig. 5, there is a gap of 0.7 eV at the X point of the 2×1 BZ, which renders the surface nonmetallic. The surface valence band edge is in almost perfect alignment with the bulk valence band maximum (VBM). So there is no band bending on this passivated surface for a p-type sample. The B band is close to the bulk valence edge. It mixes with the D_1 band near $\bar{\Gamma}$ and stays above the upper D_1 subband from X to $\bar{\Gamma}$.

The strong As–S bond found for the AsS dimer model is in disagreement with experimental findings[10,14] that S only binds to surface Ga. Replacing the top layer As with Ga can remove the As–S bonds. Also, from simple electron counting, one may expect that replacing the AsS dimer with the GaS dimer will vacate an entire surface band and the nonmetallic character will be maintained. However, from the band structure in Fig. 5, one can already see by a rigid band

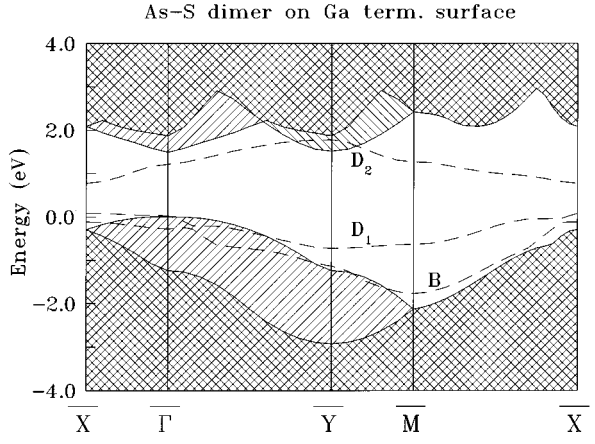

FIG. 5. Band structure of AsS dimer on Ga terminated surface. The dimer is along the [110] direction.

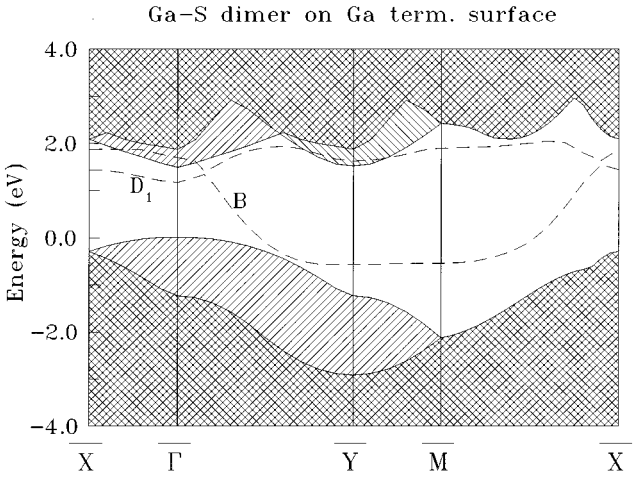

FIG. 6. Band structure of GaS dimer on Ga terminated surface.

approach that because of the overlap between the D_1 and the B bands, there may not be a gap for the GaS dimer model. Indeed, calculations show that the Ga terminated surface under GaS dimer coverage is metallic, contrary to the proposal[19] based on the simple electron counting method. Notice from Figs. 5 and 6 that the interaction between the B and the D_1 bands produces a small gap at the anticrossing point. The small size indicates that the mixture of the two bands is very weak. Because the B band is the back-bonding band and the D_1 is the lone-pair band on Ga, the wave functions of these two bands are spatially separated so the overlap, hence the interaction, between them is weak. Also, as was noted before,[19] the formation of such a structure on a clean Ga terminated surface requires a rearrangement of the top three layers of atoms, although the necessary annealing at 360 °C (Ref. 10) may help the formation of this structure. Surface band structure (see Fig. 6) shows that the weak Ga potential cannot hold down the B band, which now stays above the D_1 band in some regions of BZ. The Fermi level of this model is at 1.4 eV above the bulk VBM. This means that the band bending for a p-type sample will be substantial.

The electronic structure of the As terminated surface under GaS dimer coverage is studied in the same way (see Fig. 7). There the B band is found to be pulled down by the

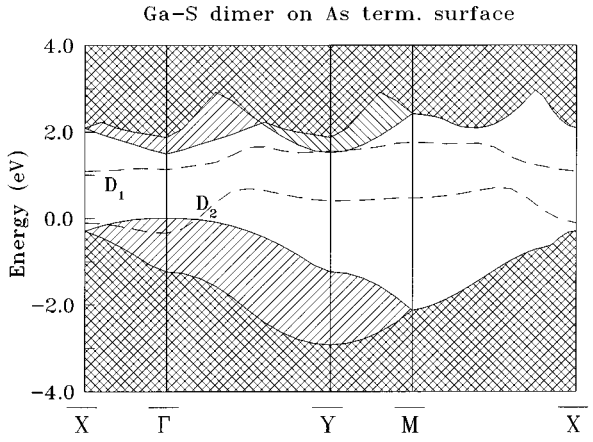

FIG. 7. Band structure of GaS dimer on As terminated surface.

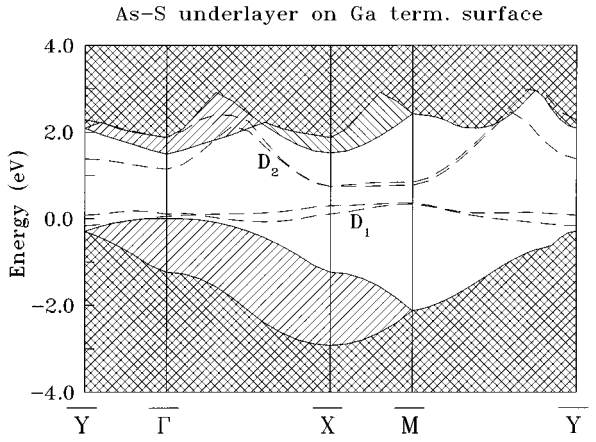

FIG. 8. Band structure of the AsS underlayer model. $\overline{\Gamma}$-$\overline{X}$ is along the [110] direction.

strong potential of the substrate As and it becomes fully occupied. The band gap on this surface is 0.4 eV. The gap is caused by the mixture and anticrossing of D_1 and D_2 bands. As expected, the potential of Ga is too weak to hold an electron lone pair, so a large part of the upper D_1 band is empty. The surface valence band edge is 0.7 eV above the bulk VBM. Similar to the case of Ga terminated surface under AsS dimer coverage, the As terminated surface under GaS dimer coverage has strong As–S bonds.

One way to construct a 2×1 model that may be nonmetallic and has no As–S bond is to cover the AsS dimer layer with a Ga layer. The Ga can break the As–S dimer bond by forming bonds with both As and S. To study this AsS dimer underlayer model, we start from the clean Ga terminated surface and replace half of the second layer As with S. The positions of the AsS dimer as well as the top layer Ga are relaxed in the calculation. The structural parameters of the AsS underlayer dimer are included in Table I. The As–S distance is large, indicating the absence of As–S bonding. The top layer Ga is found to relax outwards by 0.17 Å. There is no dimerization of the top layer Ga along the [110] direction, although weak forces on the order of 5 mRy/a.u. are observed. Interestingly, according to the convention that [110] is the direction of top layer dangling bonds, this AsS dimer under layer structure has the symmetry of 1×2. However, the low-energy electron-diffraction (LEED) pattern of the 1×2 structure is indistinguishable from that of the 2×1 structure. Only a careful LEED I-V curve analysis is able to tell the differences.

Figure 8 shows the surface electronic states of the AsS dimer underlayer model. The surface bands are two pairs of almost degenerate D_1 and D_2 bands. The degeneracy is caused by the lack of dimerization of the top layer Ga. The D_1 bands are occupied while the D_2 bands are empty. A gap of 0.4 eV is obtained on the zone boundary $\overline{X}$-$\overline{M}$. The back-bonding B band is kept well within the bulk edge by the strong potentials of the second layer S and As. The top of the surface valence band is only 0.3 eV above the bulk VBM, indicating an almost flat band on this surface.

It is well known that LDA calculations often underestimate the size of the band gaps. The calculation of the so-called quasiparticle correction requires complex and intensive computations. One of such calculations on the GaAs(110) clean surface using the GW method[27] showed that the correction moved up the conduction band by 0.8 eV while leaving the valence band unchanged. Assuming a similar quasiparticle correction for the passivated GaAs(001), one can see that the surface quasiparticle conduction bands in all three insulating cases are above the bulk conduction band edge. Since the surface valence bands for two of the structures (the AsS on Ga terminated surface and AsS underlayer surface) are almost within the bulk valence edge, these two surfaces are probably fully passivated with no surface states inside the fundamental gap.

TABLE II. Binding energies of the passivation layer, in units of eV, with reference to ideal clean surfaces and free paramagnetic atoms of the passivation layer.

S Ga term.	AsS Ga term.	GaS Ga term.	GaS As term.
4.1	7.7	7.6	6.5

From calculated total energies of various structures we have also obtained binding energies of various passivated structures, which are useful in assessing the stability of passivated GaAs(001) surfaces. The results are summarized in Tables II and III. Because different structures require different sizes of dipole layers to balance the artificial field in the vacuum region, the calculated total energies are corrected by subtracting the interaction energy between the dipole layer and the rest of the system. Another method of correction is to recalculate the total energy of the same surface structure without the dipole layer. In the case of the S covered Ga terminated surface, the difference in total energies calculated by the two methods is less than 0.08 eV. It should be pointed out that since some of the reference systems, such as free atoms, used in the calculations of binding energies are not in thermodynamic equilibrium, one must be careful when drawing conclusions based upon the results in Tables II and III.

It can be observed from Table II that S binds more strongly with Ga than with As (for the AsS on Ga terminated surface case, notice that the Ga–Ga bond is much weaker than the Ga–As bond). This is in agreement with results of an earlier thermodynamic calculation.[28] Core-level shift measurements[10,14] have also indicated that S is mostly bonded to Ga on the passivated surfaces. Table III shows the substitution energy gain for some of the passivated structures. The results indicate that when sulfur is added to the clean Ga terminated surface, the energy gains are similar for replacing either a top layer Ga or a second layer As. Given the fact that a free As atom is less stable than a free Ga atom, the AsS underlayer structure is probably more favorable thermodynamically. For As terminated surfaces, results in Table

TABLE III. Substitution energies of passivated structures, in units of eV, with reference to ideal clean surfaces and free paramagnetic atoms.

S Ga term.	AsS Ga term.	GaS As term.	AsS underlayer
1.2	1.9	0.9	0.8

III show that sulfur will replace the top layer As and form the structure of monolayer S on Ga terminated surface.

In conclusion, we have calculated the electronic structures and total energies of three 2×1 and one 1×2 passivated GaAs(001). Using hydrogen capping and a dipole layer to isolate the slab surfaces, we have performed calculations on a slab with three double layers and obtained reliable results. Our results on the S monolayer 1×1 structure are in good agreement with previous studies.[17] The binding energies of S in various structures are high, suggesting easy formation of passivation layers using sulfur-based passivation processes. However, the proposed model[19] of the Ga terminated surface under GaS dimer coverage is found to be metallic.

The other three structures of passivated surface are nonmetallic. The AsS dimer layer on Ga terminated surface gives the largest gap of 0.7 eV. Electronic structure shows no band bending on this surface, in agreement with experiments[8] that showed that sulfur passivation of As rich surface removes band bending. However, the strong As–S bond found on this surface disagrees with core level shift measurements.[10,14] The structure of the GaS dimer layer on As terminated surface may be easy to form kinematically, since most as-cleaned surfaces are Ga terminated and one only needs to replace half of the surface Ga with S.

Among the four structures studied, the AsS underlayer model is the most promising one. It is nonmetallic, has no As–S binding, and is thermodynamically favored. The surface valence band is only 0.3 eV above the bulk edge, and quasiparticle correction may push the surface conduction band out of the bulk gap. More studies, especially careful LEED measurements and analysis of I-V curves, are needed to confirm whether the AsS underlayer structure plays a significant role for sulfur-based passivation of GaAs(001). Notice that chemical processes used to clean the surface before passivation can produce very rough surfaces with a wide range of surface Ga-As ratio. The actual passivated 2×1 GaAs(001) surface could be a mixture of several structures. And the dominant structure may be sensitive to the specific passivation process.

Finally, our calculations have demonstrated the importance of first-principles calculation and illustrated the close relationship between the surface structure and the electronic properties of this interesting system. We hope this work will help us to achieve a better understanding of the structural and electronic properties, as well as the passivation mechanism of GaAs surfaces, and to devise better passivation procedures that will produce good quality GaAs(001) surfaces for electronic applications.

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