## Sulfur passivation of GaAs surfaces

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A first-principles study of the structural and electronic properties of the GaAs(111) surface with an adsorbed monolayer of sulfur atoms is presented in comparison with the previous results for the GaAs(001) surface. We determine the optimal adsorption sites of sulfur atoms and show that S atoms are more tightly bonded to Ga atoms than to As atoms. It is found that the midgap-surface-state density is remarkably reduced and the Fermi level is shifted toward the valence-band maximum by the formation of stable Ga—S bonds. The sulfur passivation of both GaAs(111) and GaAs(001) surfaces can be explained quite well in terms of the formation of Ga—S bonds on the sulfur-treated surface, without introducing any disorder or defects near the surface.

## I. INTRODUCTION

The development of GaAs technology has been impeded by the poor electronic properties of GaAs surfaces characterized by a high density of surface states. Recently, sulfide solution treatments have been reported to effectively improve GaAs surface properties.<sup>1-4</sup> The deposition of a thin Na<sub>2</sub>S film onto the GaAs(001) surface can enhance the photoluminescence (PL) intensity relative to the untreated surface.<sup>1</sup> The  $(NH_4)_2S_x$  treatment benefits the performance of minority-carrier devices sensitive to surface recombination, such as heterojunction bipolar transistor. Controllable Schottky-barrier heights are achieved on the  $(NH_4)_2S_x$ -treated GaAs(001) surface.<sup>4</sup> The sulfur treatments have been shown to passivate not only the GaAs(001) surface but the GaAs(110) and GaAs(111) surfaces as well. The  $(NH_4)_2S_x$ -treated GaAs(111) surfaces are found to be free of oxygen.<sup>5</sup> Layered transition-metal dichalcogenides (MoSe<sub>2</sub>, NbSe<sub>2</sub>) can be heteroepitaxially grown on  $(NH_4)_2S_x$ -treated GaAs(111) surfaces in spite of the large difference in their crystal structures.<sup>6</sup>

The sulfur treatments drastically reduce the surface recombination velocity to the value of the  $Al_xGa_{1-x}As/GaAs$  interface, as evidenced by the photoluminescence-yield increase. This drastic reduction was explained by Sandroff *et al.*, who assumed that the sulfur treatment had significantly lowered the surface-state density to the point that the surface Fermi level had moved toward the flat-band condition.<sup>1</sup> The surface recombination velocity, however, is not necessarily correlated with the surface-state density. In fact, direct measurements on *n*-type samples have shown that the Fermi level moves away from, rather than toward, the flat-band condition, and the band bending increases.<sup>7-9</sup>

There are two different models proposed to explain the large reduction in surface recombination velocity and the increase in band bending after sulfur treatments. On the basis of the disorder-induced-gap-state model, Hasegawa et al. have suggested that the sulfur treatment produces a negative fixed charge in the overlayer which is responsi-

ble for the band bending.<sup>7</sup> The downward band bending near the surface of *n*-type samples gives rise to a field which tends to repel electrons that may approach from the bulk region. If the absorption of photon in the PL experiment occurs mainly in the bulk GaAs away from the surface depletion region and the sites for recombination are near the surface, recombination will be effectively decreased by inhibiting carriers from transport to the surface.

Spindt et al. have discussed the electrical properties of the sulfur-treated GaAs surface in terms of the antisitedefect model of GaAs interface states.<sup>9</sup> Within this model, the high density of surface states in GaAs is attributed mainly to the presence of As- and Ga-antisite defects which are created when the surface is disrupted by an overlayer. The As-antisite defects are double-donor states at the midgap region and act as the dominant surface recombination centers. These states are compensated by double-acceptor Ga-antisite defects near the valence-band maximum (VBM), and then the position of the Fermi level is pinned between these defect states. Spindt et al. have postulated that the sulfur treatment removes excess As from the interface region, thereby reducing the number of As antisites relative to the number of Ga antisites. The reduction in the number of midgap As-antisite states will reduce the recombination center density and move the position of the Fermi level toward the VBM.

Although these models explain to some extent the electrical properties of the sulfur-treated GaAs surface, either the origin of the fixed charge in the overlayer or the mechanism of the reduction in the number of As antisites, which is the essential part of the model, is not clear. We will show in this paper that the passivating effect of sulfur treatments can be explained quite well in terms of the formation of Ga—S bonds on the treated surface, without introducing any disorder or defect near the surface.

Several studies of the structure of the sulfur-treated GaAs surfaces<sup>3,5,9,11</sup> have been motivated by their remarkably improved electronic properties. The surface-sensitive synchrotron radiation photoemission studies

have shown that the treated GaAs surface is terminated with roughly a monolayer of sulfur bonded to both Ga and As atoms, and that after annealing the As—S bonds are removed and only the Ga—S termination remains.<sup>9,11</sup> These measurements, however, cannot definitely determine the exact atomic structure of the treated surface. Within the antisite defect model, it is not the exact atomic structure but the reduction of the number of As antisites that is responsible for the improved electrical properties of the treated surface. The generation of a fixed charge is important within the disorder-induced-gap-state model. Contrary to these models, we will show that the actual bonding geometry of the sulfur-treated GaAs surface is essential for the sulfur passivation.

In this paper, we present a first-principles study of the structural and electronic properties of GaAs(111) surfaces adsorbed with a monolayer of sulfur atom. We have determined the optimal adsorption site of sulfur atoms by minimizing the total energy and have calculated the surface electronic structures for the resulting optimal adsorption configurations. The obtained results for the GaAs(111) surface together with those for the GaAs(001) surface<sup>12</sup> lead us to the understanding of the mechanism of sulfur passivation of the GaAs surface.

## **II. METHOD OF CALCULATION**

The total-energy calculations have been performed within the local-density functional formalism with use of the norm-conserving nonlocal pseudopotentials.<sup>13</sup> The exchange-correlation energy is approximated by Slater's  $X\alpha$  formalism where  $\alpha = 0.7$ . The pseudo-wave-functions are expanded in a plane-wave basis set with a kineticenergy cutoff of 7.29 Ry.

The surface is simulated by a slab geometry. The unit supercell for the GaAs(111) surface contains four GaAs layers (i.e., eight atomic layers) plus a vacuum region equivalent to about four GaAs layers in thickness. We terminate an uninteresting surface of the slab by depositing fictitious H atoms. The method of calculations will be described in detail elsewhere.<sup>14</sup>

Since our slab geometry has no inversion symmetry, an artificial electrostatic potential would be induced across the vacuum region by unbalanced dipoles at the surface. We have found that both the electronic structures and the Hellmann-Feynman forces are scarcely affected by the artificial field compared with the results obtained by using an inversion-symmetry-imposed supercell geometry.

## **III. RESULTS AND DISCUSSIONS**

We have investigated the structural and electronic properties of the GaAs(111)-(1×1) surfaces adsorbed with a monolayer of sulfur atoms. First of all, we address structure optimization. We have considered the following two possible adsorption configurations of the sulfur atoms on the GaAs(111) surface. One is the exchange configuration, where S atoms replace the outermost Ga atoms (or As atoms) of the GaAs(111)Ga surface [or GaAs( $\overline{1}$   $\overline{1}$   $\overline{1}$ )As surface], as shown in Fig. 1(a). The other is the on-top configuration shown in Fig. 1(b), where S



FIG. 1. Adsorption configurations of sulfur atoms on the GaAs(111)Ga surface: (a) the exchange site and (b) the on-top site.

atoms adsorb as adatoms onto the ideal GaAs(111)Ga surface or GaAs( $\overline{111}$ )As surface. For the As-terminated Ge(111) surface, Bringans *et al.*<sup>15</sup> have suggested that As atoms replace the outermost Ge atoms. They have argued that the on-top configuration is much less favorable energetically because an As atom is bonded to three Ge atoms in the exchange site, while it is bonded to only one Ge atom in the on-top site. On the contrary, we will show that the on-top configuration is important as adsorption geometry for a S atom on the GaAs(111) surface.

In Table I we present optimal Ga-S and As-S bond lengths for GaAs(111)Ga and GaAs( $\overline{1}\,\overline{1}\,\overline{1}$ )As surfaces adsorbed with a sulfur monolayer in the on-top and exchange sites. The adsorption energies of sulfur atoms, which are the differences between the total energy at the optimal adsorption position and that at a distant position, are also listed in Table I. In the exchange position, a S atom is threefold coordinated and establishes a single bond to each of its three neighboring Ga (or As) atoms. The optimal Ga-S (or As-S) bond length is slightly larger than the sum of covalent radii of the Ga (or As) and S atoms. As mentioned below, Ga-S and As-S bonds in the exchange site contain  $2\frac{1}{12}$  and  $2\frac{7}{12}$  electrons, respectively. The excess electrons weaken and expand these bonds by occupying an antibonding state. In the on-top position, on the other hand, S atoms are only onefold coordinated. The optimal bond lengths are a little

TABLE I. Optimal Ga—S and As—S bond lengths on the GaAs(111)Ga surface and GaAs( $\overline{1}\,\overline{1}\,\overline{1}$ )As surface with an adsorbed S monolayer in the on-top and exchange sites. Adsorption energies of S atoms, which are the differences between the total energy at the optimal adsorption position and that at a faraway position, are also listed.

Adsorption site	Bond	Length (Å)	Energy (eV)	
(111)Ga surface				
on-top $(-As \equiv Ga - S)$	Ga—S	2.11	4.02	
exchange $(-As \equiv S)$	As—S	2.40	4.32	
$(\overline{1}\overline{1}\overline{1}\overline{1})$ As surface				
on-top (—Ga≡As—S)	As—S	2.17	3.69	
exchange (-Ga=S)	Ga—S	2.41	6.07	

smaller than the sum of the atomic covalent radii. This implies that the Ga—S and As—S bonds deviate to some extent from the covalent  $sp^3$  character in the on-top configurations.

For the on-top configuration, the adsorption energy of a sulfur monolayer on the GaAs(111)Ga surface is larger by 0.33 eV per surface unit cell than that on the GaAs( $\overline{1}$   $\overline{1}$   $\overline{1}$ )As surface. For the exchange configuration, the S adsorption energy on the GaAs( $\overline{1}$   $\overline{1}$   $\overline{1}$ )As surface is larger by 1.75 eV than that on the GaAs (111)Ga surface. These results mean that the Ga—S bond is stronger than the As—S bond for both the on-top and the exchange sites. The Ga—S bond has also been found to be stronger than the As—S bond on the S-adsorbed GaAs(001) surfaces.<sup>12</sup>

From Table I, it is shown that the exchange site is energetically more favorable than the on-top site for both the GaAs(111)Ga and GaAs( $\overline{1}\,\overline{1}\,\overline{1}$ )As surfaces, as Bringans *et al.* suggested.<sup>15</sup> For S atoms to occupy the exchange sites, however, several steps are required. We take the GaAs(111)Ga surface as an example. First, a free S atom adsorbs on the outermost Ga atom on the surface, i.e., occupies the on-top site. Next, the adsorbed S atom exchanges sites with the substrate Ga atom, and the Ga atom is placed in the on-top site. Finally, the Ga atom in the on-top site is desorbed from the surface, and the adsorption of the S atom on the exchange site is completed. We present the calculated total energies for the atomic configurations appearing in the process of the S adsorption on the exchange site in Table II. It is found that large energies of about 2.0-3.0 eV are required for the exchange of the adsorbed S and the substrate Ga (or As) atoms. Desorption of the Ga and As atoms in the on-top sites also requires energies of about 1.0 eV. This indicates that it is energetically unfavorable for the S atom to move from the on-top site to the exchange site. In these calculations, we have used the energies of free atoms as the chemical potentials for the Ga and As atoms that are removed from the surface. Although it may be more realistic to choose proper reservoirs for the Ga and As atoms, the most important step in changing from the on-top to the exchange configuration (-As  $\equiv$  Ga-S  $\rightarrow$  As  $\equiv$  S—Ga) is not affected by the choice of the

TABLE II. Calculated total energies for the atomic configurations appearing in the process of the S adsorption in the exchange site of GaAs(111) surfaces, measured relative to that before the S adsorption.

Configuration	Energy (eV)		
GaAs(111)Ga surface			
$-As \equiv Ga \cdots S$	0.00		
$-As \equiv Ga - S$ (on-top site)	-4.02		
—As≡S—Ga	-0.90		
$-As \equiv S \cdot \cdot \cdot Ga \text{ (exchange site)}$	-0.08		
$GaAs(\overline{1}\overline{1}\overline{1}\overline{1})As$ surface			
$Ga \equiv As \cdot \cdot \cdot S$	0.00		
Ga $\equiv$ AsS (on-top site)	-3.69		
—Ga≡S—As	-1.98		
$Ga \equiv S \cdot \cdot \cdot As \text{ (exchange site)}$	-0.90		

atomic reservoirs, because of the same numbers of surface atoms. We thus conclude that the S atom remains on the on-top position when it adsorbs on the GaAs(111) surfaces. For the Ge(111) surface, it has been suggested that the adsorbed As atoms replace the outermost Ge atoms.<sup>15</sup> In spite of having the same surface orientation, the mechanisms of surface passivation may be quite different between the GaAs(111) and the Ge(111) surfaces.

Sulfide solution treatments involve several complicated reactions including the etching of oxide layers, sublimation of excess sulfur layers, annealing in vacuum, and so on. It is difficult to determine theoretically the resultant microscopic geometry of the adsorbed S atoms on the treated surface. The Auger electron spectroscopy measurements on the  $(NH_4)_2S_x$ -treated GaAs(111) surfaces have indicated that the S adsorption on the GaAs (111)Ga surface is more stable than that on the GaAs( $\overline{111}$ )As surface.<sup>5</sup> It is shown from Table I that the exchange adsorption site cannot explain this experimental result, whereas the on-top adsorption site is consistent with it. Therefore we suggest that the S atoms occupy the on-top sites even at the sulfide-treated GaAs(111) surface.

We show the surface electronic structure of the GaAs(111)Ga surface with a sulfur monolayer adsorbed in the optimal on-top site in Fig. 2(a). There are two surface state bands (the D1 and D2 bands) near the VBM of GaAs. These bands are associated with the sulfur dan-



FIG. 2. Electronic structures of (a) the GaAs(111)Ga surface and (b) the GaAs( $\overline{1} \overline{1} \overline{1}$ )As surface adsorbed a S monolayer in the on-top site.

gling bonds, whose directions are parallel to the surface plane, as shown in Fig. 3. On the ideal GaAs(111)Ga surface, on the other hand, there are surface states present which are associated with the Ga dangling bonds. Since the Ga potential is much shallower than the S potential, the surface states of the GaAs(111)Ga surface are located at the midgap region, much higher than those of the sulfur-adsorbed surface. That is, the adsorption of a sulfur monolayer on the on-top site of the GaAs(111)Ga surface replaces the midgap Ga dangling-bond states with the S dangling-bond states near the VBM, resulting in the shift of the Fermi level toward the VBM. The adsorption of a sulfur monolayer has also been shown to have the similar effect on the Ga-terminated GaAs(001) surface.<sup>12</sup> The Fermi-level shift is consistent with the experiments showing that the band bending for the unpassivated ntype GaAs surface is increased by about 0.2 eV after treatments.<sup>7-9</sup> The deep level transient spectroscopy measurements have shown that the midgap level in asgrown GaAs(001) samples is greatly reduced after sulfur treatments, while the level near the VBM remains with a high density.<sup>16</sup> The calculated surface-state bands are also consistent with this experiment. The surface states near the VBM will be inefficient recombination centers due to their high thermal emission probability.<sup>17</sup> Thus the surface recombination velocity will be drastically reduced after the sulfur adsorption.

The electronic structure of the GaAs $(\overline{1}\ \overline{1}\ \overline{1})$ As surface with sulfur atoms adsorbed in the optimal on-top site is shown in Fig. 2(b). The surface-state D1 and D2 bands of Fig. 2(b) are similar in characteristics to those of Fig. 2(a). The former surface bands, however, are located much higher in energy compared to the latter bands. As a result, the reduction of the midgap-surface-state density does not occur on the S-adsorbed GaAs $(\overline{1}\ \overline{1}\ \overline{1})$ As surface. On the As-terminated GaAs(001) surface, it has been found that the midgap-surface-state density is not reduced by the adsorption of a sulfur monolayer either.<sup>12</sup>

These electronic structures can be understood as follows. Since the surface S atom is only onefold coordinated in the on-top adsorption site, its bonding orbitals deviate to some extent from the  $sp^3$  character. The interaction between the S and substrate Ga (or As) atoms forms a fully filled bonding state of some  $sp_z$  character. There



FIG. 3. Charge-density contour plots of the D2 band state at the M point for the GaAs(111)Ga surface adsorbed a S monolayer in the on-top site. The plot is in a [110] plane including the Ga—As bond.

are three nonbonding orbitals remaining on the surface S atom. One orbital includes some  $sp_z$  character similar to the bonding state, which is located lower in energy and completely occupied. The other two orbitals have to some extent the  $P_x$  and  $P_y$  character. These orbitals are located higher because of their p character, and partially occupied with 2.75 (or 3.25) electrons in total for the S atom of the surface Ga-S (or As-S) bond. The surface D1 and D2 bands originate from these two dangling-bond orbitals. The bonding orbital of the S atom of the surface As—S bond deviates to a greater extent from the  $sp^3$ character, and contains more components of  $sp_z$  character than that of the S atom of the surface Ga-S bond. This is because the average valence number of S and As is 5.5 and much larger than the value of 4.0 characterizing the  $sp^3$  bonding, whereas that of S and Ga is 4.5. Consequently, the dangling bonds of the former S atom include more  $p_x$  and  $p_y$  character and are located higher in energy than those of the latter S atom. This leads to the difference in the position of the surface state bands in Figs. 2(a) and 2(b).

The  $(NH_4)_2S_x$ -treated GaAs(111) surface has been reported to be stable against oxidation, contrary to ideal GaAs(111) surfaces.<sup>5</sup> Ideal GaAs(111) surfaces have dangling bonds in the direction perpendicular to the surface plane, and the resulting surface bands have little energy dispersion. On the other hand, the S dangling bonds at the sulfide-treated surface are parallel to the surface plane, as shown in Fig. 3, and the resultant surface D1 and D2 bands have fairly large energy dispersion. These features contribute to the stability of the treated surface such as resistance to contamination, although the S dangling bonds are not completely filled.

The surface electronic structures of the GaAs(111)Ga and  $GaAs(\overline{1}\,\overline{1}\,\overline{1})As$  surfaces with a S monolayer adsorbed in the exchange site are shown in Figs. 4(a) and 4(b), respectively. There are two surface state bands, i.e., the D and A bands near the energy-gap region. We present the charge-density contour plots of these two surface band states in Fig. 5. It is shown from Fig. 5(a) that the D bands originate from the dangling orbitals of the S atoms. These bands are completely occupied in both Figs. 4(a) and 4(b), which indicates that the S dangling bonds are fully filled in the exchange site. The A band is found to be the As-S (or Ga-S) antibonding states for the Sadsorbed GaAs(111)Ga [or GaAs( $\overline{1}\,\overline{1}\,\overline{1}$ )As] surface. The As—S bond contains  $2\frac{7}{12}$  electrons, while the Ga—S bond has  $2\frac{1}{12}$ . Consequently, the A bands are occupied by 1.75 and 0.25 electrons, respectively, in Figs. 4(a) and 4(b). Because of the appearance of the A band, the S adsorption in the exchange site does not reduce the surface-state density in the midgap region of the GaAs(111) surfaces.

As shown above, the sulfur adsorption on the on-top site remarkably reduces the midgap states of the GaAs(111)Ga surface, while that on the exchange site does not. It has been also found that a sulfur monolayer effectively passivates the Ga-terminated GaAs(001) surface when it is adsorbed in the bridge position.<sup>12</sup> In this way, the sulfur atoms in the optimal adsorption site passivate both the Ga-terminated (111) and (001) surfaces by replacing the midgap Ga dangling-bond states with the S



FIG. 4. Electronic structures of (a) the GaAs(111)Ga surface and (b) the GaAs( $\overline{1} \overline{1} \overline{1}$ )As surface adsorbed a S monolayer in the exchange site.



FIG. 5. Charge-density contour plots of the D and A band states at the M point for the GaAs(111)Ga surface adsorbed a S monolayer in the exchange site. The plots are in a [110] plane including the Ga—As bond.

dangling-bond states near the VBM. Either the Asterminated (111) or (001) surfaces, however, are not passivated by the adsorption of sulfur atoms. These results indicate that the exact atomic structure of the sulfurtreated surface is essential for the sulfur passivation, contrary to the defect model's suggestion that the main factor is the gentleness of the sulfur treatment which does not disrupt GaAs samples and form high densities of defects.<sup>10</sup> We have shown that the sulfur passivation can be quite well explained in terms of the formation of Ga—S bonds on the treated GaAs surface without introducing any disorder or defect near the surface. That is, the formation of the most stable Ga—S bond reduces the surface-state density in the midgap region, resulting in a drastic reduction in surface recombination velocity.

The recent study of the synchrotron radiation photo-emission by Sugahara *et al.*<sup>11</sup> has shown that the upward band bending of *n*-type GaAs(001) surface is relaxed by the  $(NH_4)_2S_x$  treatment, contrary to the measurement by Spindt *et al.*<sup>9</sup> The controllable Schottky-barrier heights measured on the  $(NH_4)_2S_x$ -treated GaAs(001) surface may also suggest that the Fermi level for the treated surface is unpinned. However, our calculated results have shown that although the midgap surface states disappear, there are still surface states near the VBM in sufficient numbers to pin the Fermi level for the treated surface. It is an important problem to investigate whether the sulfur treatment makes the GaAs surface free of pinning or not. The surface states pinning the Fermi level near the VBM originate from the S dangling bonds. The S dangling bond is occupied by 1.75 electrons at the Ga-terminated GaAs(001) surface adsorbed with a sulfur monolayer. If there exists a proper structural modification, which makes the S dangling-bond states completely filled and induces no additional unfilled surface states, a flat-band condition is achieved for *n*-type GaAs(001) surfaces. It has been found that the formation of S-S dimer cannot significantly change the Fermi-level pinning condition.<sup>12</sup> The change in the coverage of sulfur atoms can be one candidate for the structural modification. Although we have assumed the adsorption of a S monolayer so far, the S coverage of sulfur-treated surfaces is not so definitely determined experimentally. If  $\frac{1}{4}$  monolayer of S atoms is assumed to be additionally deposited on the GaAs(001) surface adsorbed with a sulfur monolayer, for example, it would be possible that the dangling bonds of all S atoms including the additionally deposited ones are fully filled. The deposition of more than  $\frac{1}{4}$  monolayer would be energetically unfavorable because of the filling of antibonding states. For the GaAs(111) surface we have not found a promising modification yet. Further experimental and theoretical studies are needed to determine whether the sulfur-treated surface is free of pinning or not.

In conclusion, we have investigated the structural and electronic properties of GaAs surfaces adsorbed with a monolayer of sulfur atom using the *ab initio* pseudopotential method. We have determined the optimal adsorption sites of sulfur atoms, and shown that S atoms are more tightly bonded to Ga atoms than to As atoms. Sulfur adsorption can noticeable reduce the surface-state density in the midgap region of the Ga-terminated GaAs surfaces. But the reduction does not occur on the Asterminated surfaces. The passivating effect of sulfur treatments can be explained quite well in terms of the formation of stable Ga—S bonds on the treated surface. Sulfide solution treatments include much more complicated reactions than the adsorption of sulfur atoms, and the treated surfaces are not necessarily the ordered GaAs surfaces adsorbed with a sulfur monolayer. The present findings, however, provide a microscopic understanding of the effect of the sulfide treatments on the GaAs surfaces, and suggest that such treatments can effectively passivate the GaAs(111) as well as GaAs(001) surfaces.

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