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Ab initio study of atomic geometry, electronic states, and bonding for H_2S adsorption on III-V semiconductor (110)-(1×1) surfaces

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Ab initio calculations, based on pseudopotentials and the density-functional theory, have been made to investigate the equilibrium atomic geometry, electronic states, and bonding of the H_2S molecule on the InP(110), GaAs(110), and GaP(110) surfaces within a dissociative adsorption model. In general, the adsorption of H_2S on the three semiconductors shows similar behavior. The calculated average distances between the topmost InP, GaAs, and GaP layer and the sulfur atom are 1.87, 1.67, and 1.65 Å, respectively. In all the cases studied here, the fundamental band gap is free of surface states, with an occupied surface state close to the valence-band maximum. The calculated electronic states are in agreement with reported angle-resolved photoemission data. [S0163-1829(98)04208-8]

I. INTRODUCTION

The determination of the surface atomic structure and its relation to electronic properties plays a significant role in modern surface science and technology. A GaAs surface exposed to air shows poor electronic properties, due to a high density of surface states pinning the Fermi level in the middle of the band gap. Recently it was shown[1–5] that the electronic properties of the (100), (110), and (111) surfaces of GaAs improve significantly upon sulfide treatment. In general three different types of sulfur sources have been used: treatment with a solution of $Na_2S\cdot 9H_2O$ (Ref. 6) or $(NH_4)_2S_x$,[4,5,7] treatment with H_2S gas,[1–3,8–11] and using S from a solid state source in ultrahigh-vacuum conditions.[12]

The adsorption of H_2S on III-V(110) was studied extensively using low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPS). In early studies using LEED, AES, and angle-resolved UPS, Williams and co-workers[8,13] reported that exposure to H_2S resulted in an ordered overlayer on InP(110). They proposed that for low exposures the room-temperature adsorption of H_2S on InP(110) was mostly molecular, and found that the molecule easily desorbed upon heating the sample. From the AES and UPS studies, Kuhr, Ranke, and Finster[1] and Ranke and co-workers[2,3] concluded that, at 150 K, H_2S is adsorbed on GaAs(110) either as a molecule or as partially dissociative species like SH^- and H^+ on the anion surface atoms, leaving the surface cations essentially unaffected. (Their work also concluded that, at 720 K, atomic sulfur is adsorbed which begins to penetrate into the lattice for higher exposures.) However, from the core-level photoemission results Ranke and co-workers[2,3] could not conclude what is the correct form of H_2S adsorption—molecular or dissociative.

Recently the adsorption of H_2S on III-V(110) was studied in detail by Dudzik and co-workers[9–11,14] using core-level x-ray-photoelectron spectroscopy (SXPS), the normal-incidence x-ray standing wave (NIXSW), valence-band angle-resolved UPS (ARUPS), and LEED. They reported that the adsorption of H_2S occurs at room temperature on InP(110) and GaP(110), but only at low temperatures (200 K or below) on GaAs(110). From studies of all the spectral changes and temperature effects, they firmly proposed a *dissociative adsorption model* for H_2S on the three surfaces, consistent with a (1×1) LEED pattern. According to their model, the H_2S molecule dissociates into a SH^- radical and a H^+ ion, with H^+ bonded to P and SH^- located in the anion site of the continued-layer structure, bonded to the surface cation. The dissociative molecular model is supported by the observation that the reactivities of different III-V semiconductors scale with the proton affinity of the anion dangling bond.[11]

In the present work we report *ab initio* theoretical investigations of the atomic geometry, electronic states, and bonding of H_2S on III-V(110) using the dissociative molecular geometry proposed by Dudzik and co-workers. From our total-energy calculations we propose a slight modification to the orientation of the SH^- radical over the model proposed by Dudzik and co-workers.

II. METHOD

Our calculations are based on the application of the *ab initio* pseudopotential method.[15] We consider an artificially constructed periodic geometry along the surface normal. The unit cell included an atomic slab with seven layers of III-V substrates and then H_2S molecules on each side of the slab, and a vacuum region equivalent of six substrate atomic layers. The electron-ion interaction was considered in the form of *ab initio* norm-conserving pseudopotentials.[16] The electron-electron interaction was considered within the local-density approximation (LDA) of the density-functional theory, with the correlation scheme of Ceperley and Alder.[17] The H_2S/III-V(110)-(1×1) interface was modeled by considering the following structure: the H^+ ion located along the surface anion dangling bond and the SH^- radical located in the anion site of the continued-layer structure, bonded to the surface cation. However, two different orientations for the H^- ion in the SH^- radical were tried, as shown in Fig. 1 (referred to as models I and II).

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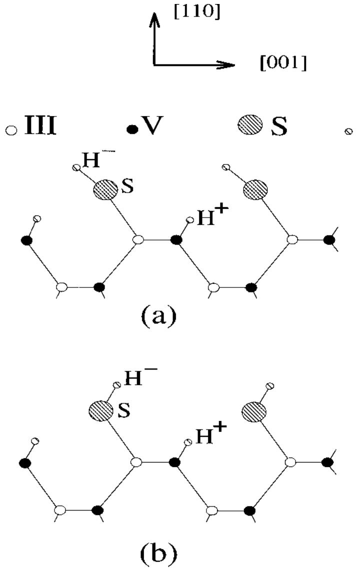

FIG. 1. Schematic side view for the H_2S adsorption on III-V(110). (a) Model I was proposed by Dudzik *et al.* (Ref. 11). (b) Model II is proposed by us.

Single-particle wave functions were expanded on a plane-wave basis. Self-consistent solutions to the Kohn-Sham equations were obtained by employing a set of four special **k** points.[18] For geometry optimization, plane waves were considered up to a kinetic energy cutoff of 8 Ry. This cutoff was found to be adequate for structural studies. For example, when the cutoff energy is increased to 10 Ry the key structural parameters, such as In-S bond length and the vertical distance between the overlayer S and the substrate layer, change by less than 0.5%. The adequacy of 8-Ry cutoff was also established in a previous paper on a similar system.[19] However, once the optimum geometry had been determined, a cutoff of 12 Ry was used to obtain well-converged band structure and bonding results.

III. RESULTS AND DISCUSSIONS

Our calculated equilibrium lattice constants for bulk InP, GaAs, and GaP are 5.67, 5.50, and 5.35 Å, respectively. These values are in agreement with other theoretical studies[20] using the pseudopotential method, and were used in performing the surface calculations. Geometry optimization is achieved by minimizing the total energy[15] with the help of Hellmann-Feynman forces. The resulting atomic geometries and band structures will be described and compared with the existing experimental results in the following sections.

The H_2S/III-V(110) interface was modeled by considering two different dissociative molecular geometries within the continued-layer structure. In both geometries the proton H^+ is bonded to the surface anion (i.e., P or As) along the dangling-bond direction, and the SH^- complex is bonded to the surface cation (i.e., In or Ga). In model I, while the S atom lies along the cation dangling-bond direction, the H^- ion is located in the direction suggested by Dudzik *et al.*,[11] as shown in Fig. 1(a). Our energy minimization procedure, starting with this geometry, suggested that the H^- ion would move in the direction opposite to that suggested by Dudzik *et al.* This led us to consider model II, with the H^- ion located along the dangling-bond direction of the S atom in the continued-layer structure, as shown in Fig. 1(b). As possible geometries, we considered a number of different orientations of H^- bonded to S. As the orientation is changed from that for model II toward model I, the total energy of the system increases. We find that model I is unstable, lying at an energy 1.2 eV higher than model II for H_2S/InP(110). Similar findings were made for the other two surfaces. Model II was subsequently used in all the cases studied here.

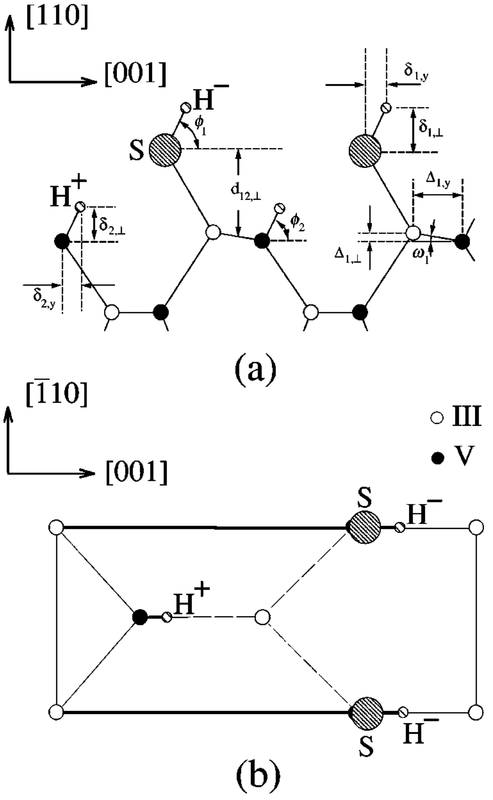

FIG. 2. Schematic relaxed atomic geometry for model II of H_2S adsorption on III-V(110): (a) side view and (b) top view.

It is well known that the relaxation pattern of clean III-V(110) surfaces is characterized by an outward (inward) movement of the surface anion (cation), with a tilt in the surface layer in the range 27°–29°.[20] Our calculations (for model II) reveal that upon H_2S adsorption all the three surfaces are derelaxed, acquiring a very small counter relaxation: the surface cation (anion) has moved outward (inward) by a small amount. Figure 2 shows schematic relaxed top and side views of model II, and indicates the key structural parameters. The calculated relaxed atomic geometrical parameters are listed in Table I. We will discuss the three surfaces individually.

A. H_2S deposition on InP(110)

Using the same pseudopotential method as in this work, it was found earlier[15] that on InP(110) the top layer tilts by 27.1° and the second layer tilts by −3.1° (the negative sign indicates tilt in the opposite direction). Upon H_2S adsorption, the tilt of the top InP(110) layer is changed to −7°, and its vertical buckling ($\Delta_{1,\perp}$) is reduced to 0.19 Å . These values are only a little different from those for the second layer on the clean InP(110) surface. Thus the adsorption of

TABLE I. Structural parameters (in Å) of model II (cf. Fig. 2) for the H_2S adsorption on InP(110), GaAs(110), and GaP(110) surfaces.

	$d_{12,\perp}$	$\delta_{1,\perp}$	$\delta_{1,y}$	$\delta_{2,\perp}$	$\delta_{2,y}$	$\Delta_{1,\perp}$	$\Delta_{1,y}$	ϕ_1(deg)	ϕ_2(deg)	ω_1(deg)
InP	1.87	1.33	0.36	1.00	1.80	0.19	1.54	74.85	29.05	−7.03
GaAs	1.67	1.28	0.55	1.14	2.03	0.15	1.37	66.75	29.32	−6.37
GaP	1.65	1.29	0.57	1.10	2.05	0.12	1.31	66.20	28.22	−5.23

H_2S has practically derelaxed the InP(110) surface. We find that the perpendicular distance ($\delta_{2,\perp}$) between P and H^+ is about 1.00 Å, and the d(P-H^+) bond length is the same as the sum of the corresponding covalent radii, 1.40 Å.[21] The perpendicular distance ($\delta_{1,\perp}$) between S and H^- is 1.33 Å, and the bond length value of 1.38 Å for d(S-H^-) is 3% larger than the sum of the corresponding covalent radii. The calculated perpendicular average distance $d_{12,\perp}$ between the sulfur atom and the topmost InP layer is 1.87 Å. This result is in good agreement with the value of 1.97 Å determined from the XSW measurement by Dudzik *et al.*:[11] the difference is at least partly due to the theoretical lattice constant being 3.5% smaller than the experimental value. It is also interesting to note that the calculated value of $d_{12,\perp}$ for H_2S/InP(110) is very close to the corresponding value for the S/InP(110) system calculated in a recent theoretical study[19] (1.98 Å), and determined from XSW measurements (1.95 Å).[12] The calculated bond length d(In-S) is 2.61 Å, approximately 5% larger than the sum of the covalent radii of In and S.[21]

From NIXSW studies Dudzik *et al.*[11] determined the offsets of the S atom from the ideal continued-layer phosphorus site. They found that these shifts are 0.02 ± 0.08 Å, −0.04 ± 0.05 Å, and −0.10 ± 0.06 in the [$\bar{1}$10], [001], and [110] directions, respectively. Our calculated offsets are somewhat different from these values. We find that the sulfur atom shifts by −0.37 Å in the [001] direction, and by 0.02 Å in the [110] direction from the ideal continued-layer structure phosphorus site. There is no shift in the [$\bar{1}$10] due to the symmetry present on the (1×1) surface. The calculated shift along [001] agrees in sign but is larger than the NIXSW value. Neither the sign nor the magnitude of the calculated shift in the surface-normal direction [110] agrees with the NIXSW determination.

The ARUPS data obtained by Dudzik *et al.*[14] indicated up to six surface-related bands in the binding-energy range 0–7 eV. Three of these, labeled α,β, and γ, were identified as adsorbate related. While not making a clear identification, Dudzik *et al.*'s work seemed to indicate that the feature labeled β is a SH line, following the investigation of H_2S/Si(100) by Schröder-Gergen and Ranke.[22] A fourth band, labeled X_3, is considered to originate from the adsorption-enhanced bulk density of states. However, the authors were uncertain about the orbital nature of these states.

We identify a total of five occupied electronic states, as shown in Fig. 3. Also shown in that figure are the ARUPS data obtained by Dudzik *et al.*[14] The experimental spectra were rigidly shifted upwards by 0.5 eV to show a maximum level of correspondence with theory. The electronic total charge-density plots in vertical planes containing the P-H^+ and S-H^- bonds are shown in Figs. 4(a) and 4(b), respectively. The orbital features of the individual states at the $\bar{M}$ point are shown in Fig. 5. As seen in Fig. 4(a), the In-P bonding at the interface is partly covalent and partly ionic, similar to that in bulk InP. The In-S bonding is also partly covalent and partly ionic, but is stronger than the In-P bonding. The P-H^+ and S-H^- bondings show some covalency and pronounced ionic character.

The occupied state S_1 lies below the bulk valence-band continuum. This state shows covalent bonding between the s orbital of the H^- ion and the s orbital of the surface S atom, as shown in Fig. 5(a). In the binding energy range 2–6 eV, we obtain three states, labeled S_2, S_3, and S_4, which are clearly seen in the stomach gap region. While the ARUPS data[14] indicates the band γ almost resonant with bulk at the upper end of the ionic gap, we do not find any surface states in that region. From Figs. 3 and 5(b) we note that the state S_2 is resonant with bulk, and has a pronounced contribution from the second-layer In atoms, as found on the clean InP(110) surface, but also has some contribution from the surface PH^+ and SH^- complexes. Therefore, this state is a surface state modified by the dissociative adsorption of H_2S. This state can be compared to the band labeled X_3 in the ARUPS studies by Dudzik *et al.*[14] In the middle of the stomach gap we identified two closely lying bands, labeled S_3 and

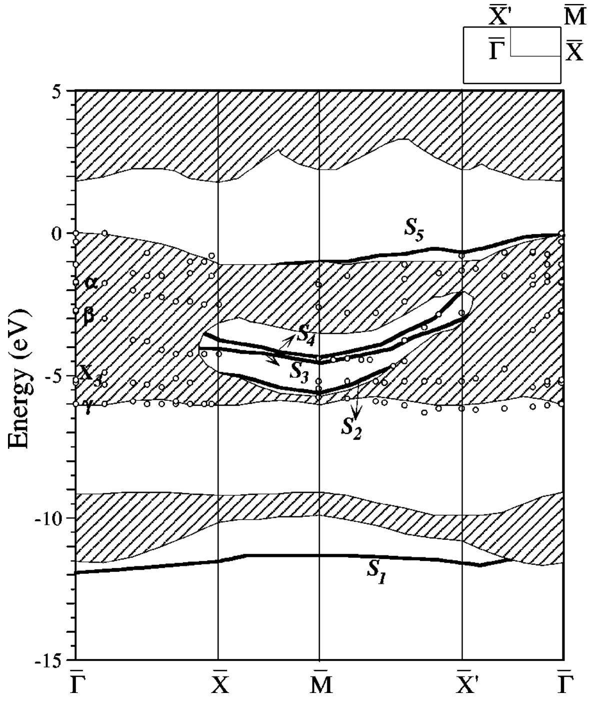

FIG. 3. Electronic band structure of the InP(110)-H_2S interface. The projected bulk spectrum is shown by hatched regions. The calculated electronic states are shown by thick curves and the experimental results of Dudzik *et al.* (Ref. 14) are indicated by open symbols. The experimental data have been rigidly shifted upwards by 0.5 eV, as discussed in the text.

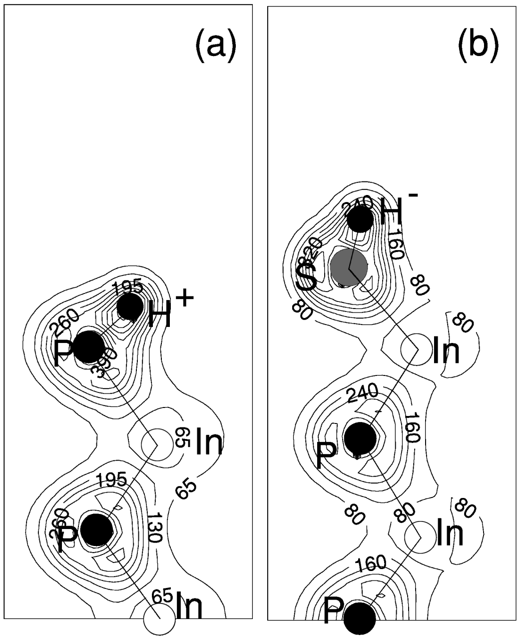

FIG. 4. Electronic total charge-density plots of the InP(110)-H_2S interface in (a) a vertical plane containing the P-H^+ bond, and (b) a vertical plane containing the S-H^- bond. The contour values are normalized to 72 electrons per unit-cell volume of 631.26 Å^3.

S_4. The energy location and dispersion of the experimentally measured band β matches with both these bands, in particular the S_3 band. However, we do not agree with the description of the orbital nature of the experimental band β forwarded by Dudzik *et al.* We find that the state S_3 is made of the back bond orbital of the surface S atoms and the *s* orbital of the hydrogen ion in the vertical plane containing the S-H^- bond, as shown in Fig. 5(c). State S_4 is a P-H^+ bonding state, made of the dangling bond of the P atom and the *s* orbital of H^+, as shown in Fig. 5(d). The experimentally measured band α can be matched with our state S_4 around the $\overline{X'}$ point. The highest occupied state lies very close to the edge of the bulk region in the fundamental gap, labeled S_5, due to the *p* orbital of the S atoms, shown in Fig. 5(e). It is interesting to note that this adsorbate state lies roughly at the same energy position as the P-derived dangling-bond state on the clean InP(110) surface. This is not surprising, as in the dissociative model the SH^- complex plays the role of anion on the clean surface. In the experimental ARUPS data there are features which can be matched with our S_5 state along $\overline{\Gamma}$-$\overline{X'}$-$\overline{M}$. We do not find any unoccupied electronic states in the fundamental band gap, which therefore remains free of surface states.

Our analysis of the states, therefore, indicates that within the dissociative model adsorption of H_2S on InP(110) leads to S *p*-like (S_5), SH^--like (S_1 and S_3) and PH^+-like (S_4) states, and the PH^+ and SH^- complexes modify the surface state S_2 on the clean surface originating from the second-layer cation.

B. H_2S deposition on GaAs(110)

For the adsorption of H_2S on GaAs(110), the structural and electronic results should be considered in the same way as the adsorption on the InP(110) surfaces. In this system, the *d*(Ga-As) bond length is about 2% smaller than the sum of the corresponding covalent radii, in agreement with the calculated lattice constant. The calculated tilt angles of the top two atomic layers on clean GaAs(110) surface are 30.2° and −3.9°, respectively.[15] H_2S deposition changes the tilt of the top-layer GaAs(110) to −6.4°, with a vertical buckling $\Delta_{1,\perp}$ of 0.15 Å. The *d*(Ga-S) bond length is 2.20 Å, about 4% smaller than the sum of the corresponding covalent radii. The *d*(S-H^-) bond length is 1.40 Å, the same as on H_2S/InP(110). The *d*(As-H^+) bond length is 1.54 Å. The perpendicular distance $\delta_{2,\perp}$ between As and H^+ is 1.14 Å, and the perpendicular distance $\delta_{1,\perp}$ between S and H^- is 1.28 Å. The perpendicular average distance between the sulphur atom and the topmost layer of the GaAs surface is 1.67 Å. This value is smaller than the value of 1.87 Å for InP.

We identify five occupied electronic states which are labeled S_1 to S_5, as in the case of InP, and shown in Fig. 6. The electronic total charge-density plots show the same bonding characteristics as for the H_2S/InP(110) system. In addition, we note that the Ga-S bonding is stronger than the Ga-As bonding. The occupied state S_1 lies below the bulk valence band, and is due to the covalent bonding between the *s* orbitals from the adsorbate S atom and the H^- ion. As in the case of H_2S/InP(110), the state S_2 is primarily localized on Ga atoms at the second GaAs layer, but also receives some contribution from the PH^+ and SH^- complexes. It is a resonant state, with its energy close to the lower edge of the stomach gap.

The experimental study by Dudzik *et al.*[10] indicated that in the binding energy range 2–8 eV there are up to three features which can be associated with the adsorption of H_2S. One of these lies in the ionic band gap at approximately the binding energy of 7.5 eV at $\overline{\Gamma}$, $\overline{X}$, and $\overline{X'}$. We do not find any state in the ionic gap. The two other features observed experimentally at $\overline{X}$ can be compared with our states S_3 and S_4. Similarly, the state observed experimentally at approximately 2.5 eV binding energy at $\overline{X'}$ can be compared with our state S_4. We find that the dispersion as well as the orbital characteristics of the states S_3, S_4, and S_5 for H_2S/GaAs(110) are identical to those for H_2S/InP(110). The highest occupied adsorbate-induced state S_5 is seen as a rather flat band just above the bulk valence-band continuum around the $\overline{X'}$ point. We do not find unoccupied states in the fundamental gap. There is a band gap (within the local-density approximation) of about 1.40 eV at $\overline{\Gamma}$, which is very close to the low-temperature experimental value of 1.52 eV.[23] This close agreement between the LDA band gap and the experimental value is due to the smaller theoretical lattice constant used in our work.

C. H_2S deposition on GaP(110)

The adsorption of H_2S on GaP(110) is similar to that on InP(110), but seems to be somewhat more rapid.[10] Therefore we used the same starting model (i.e., Model II) as in our InP and GaAs studies in order to calculate the geometrical parameters and electronic structure of the H_2S/GaP(110)

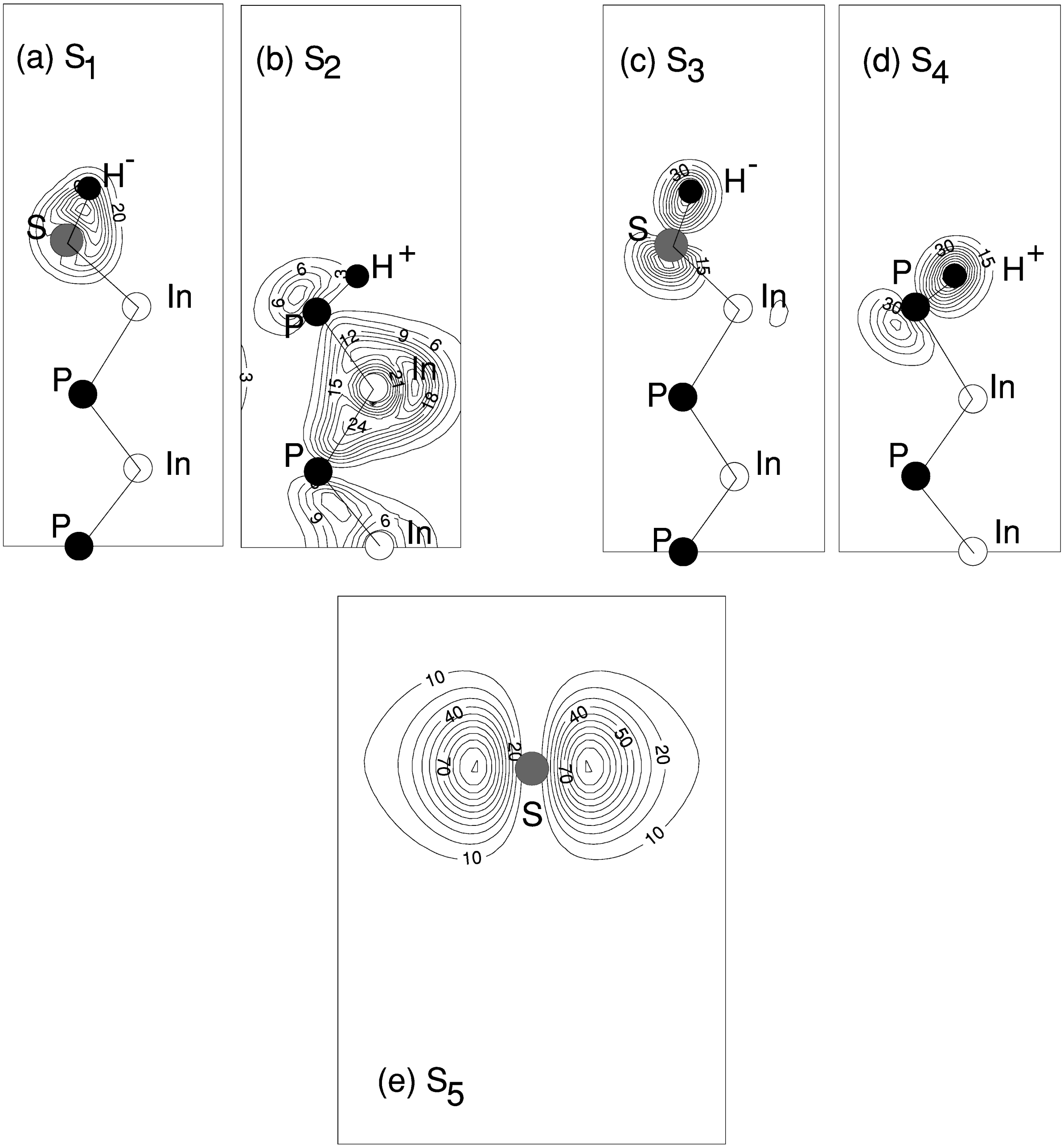

FIG. 5. Electronic charge-density plots for individual surface states for the relaxed geometry of the InP(110)-H_2S interface: (a) S_1 at $\overline{M}$, (b) S_2 at $\overline{M}$, (c) S_3 at $\overline{M}$, (d) S_4 at $\overline{M}$, and (e) S_5 at $\overline{M}$ in a horizontal plane. The contour values are normalized to two electrons per unit cell volume of 631.26 Å^3.

surface. The results are similar to those obtained for the H_2S/InP(110) and H_2S/GaAs(110) systems. Again, we note that the Ga-S bonding is stronger than the Ga-P bonding.

The clean GaP(110) surface is characterized[24] by a tilt of the top layer by 27.6° and a vertical buckling of 0.58 Å. The second layer shows a tilt of -3.2°. Upon H_2S adsorption the tilt of the top GaP layer becomes -5.23°. Thus, similar to GaAs and InP, the GaP top layer is not only derelaxed but also shows a small amount of counter-relaxation. The calculated perpendicular average distance between the sulfur atom and the topmost GaP layer is 1.65 Å. The $d(\text{S-H}^-)$ and $d(\text{P-H}^+)$ bond lengths are 1.41 and 1.49 Å, respectively.

For the H_2S/GaP(110) system we observe five surface states, as shown in Fig. 7. Their orbital characteristics are similar to the corresponding states obtained for the other two systems. The state S_1 is clearly split off below the bulk valence band. The state S_2 lies at the upper edge of the ionic gap in GaP. The states S_3 and S_4 lie in the middle of the stomach gap. Once again, their orbital characteristics, shown in Fig. 8, are similar to those for the other two systems. Finally, the highest occupied surface state S_5 is only seen just above the bulk valence-band continuum around $\overline{X}'$. We do not find any unoccupied states in the fundamental gap either. There is a band gap (within the local-density approximation) of about 1.8 eV at Γ, which is ~0.50 eV smaller than the experimental value.[23]

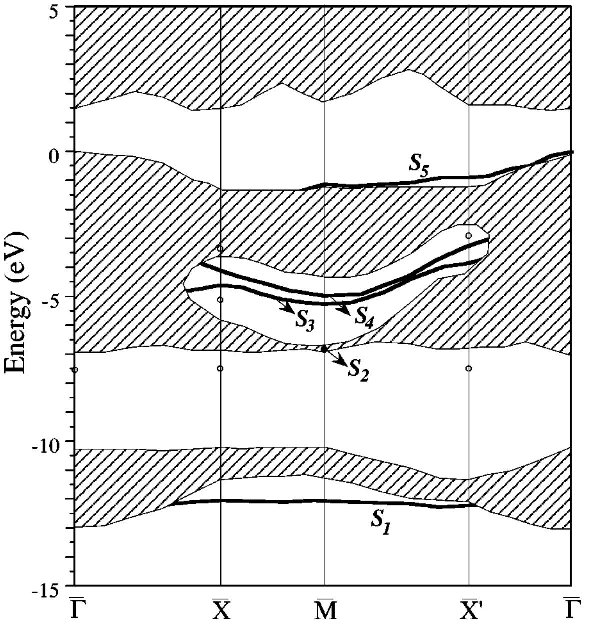

FIG. 6. Electronic band structure of the GaAs(110)-H_2S interface. The projected bulk spectrum is shown by hatched regions. The calculated electronic states are shown by thick curves and the experimental results of Dudzik *et al.* (Ref. 11) are indicated by open symbols.

D. Discussion of results for H_2S adsorption on InP, GaAs, and GaP

From the results presented above, we can obtain certain trends in structural and electronic properties of H_2S adsorption on III-V(110) surfaces. The first point we notice is that, upon H_2S adsorption, the top atomic layer of InP(110) exhibits a larger counter-relaxation than do the GaAs(110) and GaP(110) surfaces. Second, the vertical distance between the S atom and the topmost substrate layer, $d_{12,\perp}$, is much larger for InP(110) than for GaAs(110) or GaP(110). We also find that the vertical distance between H^+ and its neighboring anion, $\delta_{2,\perp}$, is much smaller for InP(110) than for GaAs(110) and GaP(110). However, the vertical distance $\delta_{1,\perp}$ between the H^- ion and the S atom in the SH^- complex remains constant within 0.05 Å for all the systems studied here.

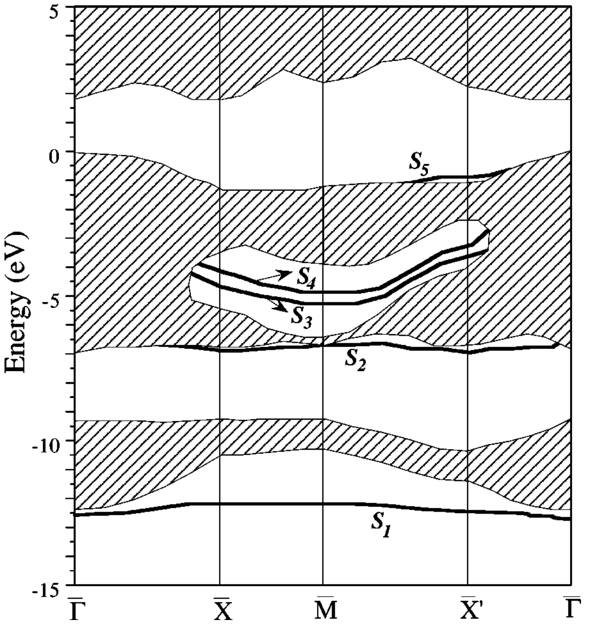

FIG. 7. Electronic band structure of the GaP(110)-H_2S interface. The projected bulk spectrum is shown by hatched regions, and the electronic states are shown by thick curves.

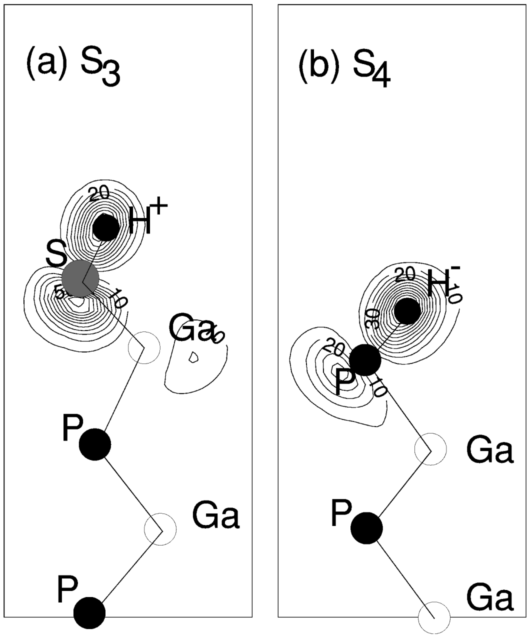

FIG. 8. Electronic charge-density plots for individual surface states for the relaxed geometry of the GaP(110)-H_2S interface: (a) S_3 at $\bar{M}$. (b) S_4 at $\bar{M}$. The contour values are normalized to two electrons per unit-cell volume of 631.26 Å^3.

The electronic state S_1 derived from the S-H^- bonding is located in the binding-energy range 12.0–12.5 eV below the bulk valence-band maximum for all three substrates. The mainly cation-derived state S_2 lies at $\bar{M}$ at approximately −6.75 eV for Ga substrates (i.e., GaAs and GaP) and at approximately −5.5 eV for In substrate (i.e., InP). The state S_3 (which is a cation-SH^- bonding state) lies at $\bar{M}$ at −4.5 eV for InP substrate, and at −5.25 eV for GaAs and GaP substrates. This difference in the energy location of the S_3 state can be understood on the basis of its cation-SH^- bonding nature. Similarly, we find that the state S_4 lies at the same energy at $\bar{M}$ for the GaAs and GaP substrates, but is pushed upwards by 0.5 eV for the InP substrate. This energy difference between the In and Ga compounds is much smaller than the difference for the S_3 state. This is not surprising as the S_4 state is anion-H^+ derived. The state S_5 derived from *p* orbitals of the S atom shows a similar dispersion pattern for the three substrates.

Investigations of the total electronic charge-density plots suggest that the In-S bond is stronger than the In-P bond, the Ga-S bond is stronger than the Ga-P and Ga-As bonds, and the In-S bond is slightly stronger than the Ga-S bond. As expected, the S-H^- and anion-H^+ bondings are rather similar for the three substrates.

IV. SUMMARY

Using an *ab initio* pseudopotential calculation, we studied the atomic geometry, electronic states and bonding of H_2S

adsorbed onto InP(110), GaAs(110), and GaP(110) semiconductor surfaces. Starting with the dissociative molecular model proposed by Dudzik *et al.*, we arrived at a slightly different bonding configuration of the molecule: the SH^- ion is located in the anion site of the continued-layer structure, bonded to the surface cation, and the H^- ion is bonded to the surface S atoms along the dangling bond direction. The adsorption of the molecule generates a small amount of counter-relaxation of the topmost layer of the substrate.

The calculated average distance between the S atom and the topmost substrate layer is 1.87, 1.67, and 1.65 Å for the InP, GaAs, and GaP substrates, respectively. The calculated result for H_2S/InP is in excellent agreement with the experimental value of 1.90 Å obtained by Dudzik *et al.*[11] As can be expected, the S-H^- bond length is almost the same for the three substrates: 1.38, 1.40, and 1.41 Å for InP, GaAs, and GaP, respectively. The S-H^- and the anion-H^+ bonds are partly covalent and partly ionic. The calculated electronic states originating from S-H^- and anion-H^+ bondings are in good agreement with photoemission results obtained by Dudzik *et al.*[14] For all the three adsorbate systems the bulk band gap is free of surface states. Thus we expect that the adsorption of H_2S on other III-V semiconductors would have the same passivation behavior.

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