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First-principles calculations of molecular- and atomic-hydrogen reactions on As-terminated GaAs(100) surfaces

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We have investigated the reaction of molecular and atomic hydrogen on an As-terminated GaAs(100) surface, on which As dimers exist, by performing a first-principles total-energy calculation. According to the present calculations, the H_2 molecule neither dissociates nor sits on the surface while the H atoms sit on several sites accompanied by As-dimer distortion. The As-dimer distortion is well described by the simple electron counting model, taking orbital energies into consideration. We have also found that the total energy of the H-atom-adsorbed surface is comparable to that of the GaAs(100) 2×4 surface exposed to arsine and hydrogen gases.

I. INTRODUCTION

Molecular and atomic hydrogen is inevitably introduced into the reaction chamber during the crystal growth of GaAs, since most sources of GaAs contain H atoms in the molecules. Hydrogen decomposed from the sources is considered to play several important roles, such as surface cleaning,[1] growth-rate controlling,[2] and passivation of deep or shallow levels.[3] However, despite the importance of the hydrogen reaction on GaAs, microscopic knowledge of this system is still poor.

Hydrogen adsorption on GaAs has been studied by means of electron-energy-loss spectroscopy, and the vibrational models of surface Ga-H and As-H species have been observed.[4–7] However, the adsorption sites cannot be determined directly from the experimental data. Theoretical work has been done to investigate the H-atom adsorption and accompanying surface reconstruction on the GaAs(110) surface[8] but not yet on the GaAs polarized surfaces, e.g., the (111) and (100) surfaces.

In addition to the technological motivation, the hydrogen reaction is of fundamental interest in understanding the physics and chemistry of GaAs surfaces. It is well known that the atomic structure of the GaAs(100) 2×4 surface, i.e., three As dimers with one missing dimer per unit cell, is explained by the simple electron counting model.[9] This model requires the surface to have nonmetallic electronic structures; all Ga dangling bonds and As dangling bonds are required to be empty and to be fully occupied, respectively. However, hydrogen adsorption on the Ga or As sites may destroy this condition. A fundamental question arises as to whether the electron counting model can be extended to the cases of adsorbates on GaAs surfaces. Although the electron counting model has already been used to calculate the atomic structure of the S-adsorbed GaAs(100) surface within a semiempirical tight-binding method,[10] it has not been proven that this counting model is reliable when a first-principles calculation is performed.

In this paper, we focus our attention on the As-terminated GaAs(100) surface, which is made by growing with high arsine pressure. We have performed a first-principles band-structure total-energy and force calculation in order to investigate the reaction of hydrogen with the As-terminated GaAs(100) surface, on which As dimers exist, by assuming that the coverages of surface As and H atoms are 1 and 0.5 monolayers (ML's), respectively. To our knowledge, this is the first band-structure calculation of the hydrogen on the polarized GaAs surface. According to this calculation, the GaAs(100) surface without hydrogen adsorption is metallic. Furthermore, we have found that molecular hydrogen neither dissociates nor sits on the GaAs surface. This is because there is a large gap between the level locations of H_2 molecular orbitals and those of the valence orbitals of surface As atoms, which hinders the hybridization of H and As covalent orbitals. On the other hand, atomic hydrogen has been found to sit on several sites of the As-terminated GaAs(100) surface resulting in the surface As dimers being preserved but slightly distorted from their usual positions. The H-atom adsorption has been found to change the surface to a nonmetal. We have also found that the resulting distortions of the As dimers are explained by the electron counting model combined with simple consideration of the orbital energy of a lone pair on each surface As site. Therefore, we have concluded that the simple electron counting model can be extended to the case of H-atom adsorption on GaAs surfaces. Finally, the stability of the H-adsorbed GaAs(100) surface has been found to be comparable to that of the GaAs(100) 2×4 surface exposed to arsine and hydrogen gases.

This paper is organized as follows: The details of the calculation are presented in Sec. II. The results for the molecular and atomic hydrogen reactions on the As-dimerized GaAs(100) surface are shown in Secs. III and IV, respectively. The comparison of the total energy of the H-covered surface with that of the 2×4 surface is presented in Sec. V. A summary and discussion are given in Sec. VI.

II. CALCULATION

We have performed a first-principles total-energy band-structure calculation within the framework of the local-density approximation (LDA). In this calculation, we have used hard norm-conserving nonlocal pseudopotentials constructed using the method of Bachelet, Hamann, and Schlüter.[11] For the wave-function expansion, we have used a Gaussian basis set. We have used three exponents for Ga 4*s*, i.e., 0.14, 0.34, and 0.82 $(\text{a.u.})^{-2}$, and two for Ga 4*p*, i.e., 0.14 and 0.24 $(\text{a.u.})^{-2}$, and one for Ga 4*d*, 0.18 $(\text{a.u.})^{-2}$. For the As atom, we have used three exponents for As 4*s*, i.e., 0.14, 0.53, and 089 $(\text{a.u.})^{-2}$, two for As 4*p*, i.e, 0.14 and 0.31 $(\text{a.u.})^{-2}$, and one for As 4*d*, i.e., 0.18 $(\text{a.u.})^{-2}$. For the H atom, we have used three exponents for the H 1*s* orbital, i.e., 4.500 38, 0.681 28, and 0.151 37 $(\text{a.u.})^{-2}$. All of these Gaussian exponents were determined by fitting to numerically obtained pseudoatomic orbitals. For the exchange and correlation energies in the LDA, we have used the analytic form[12] of the numerical result of Ceperlay and Alder.[13] In order to carry out the geometry optimization of the atomic configurations, we have calculated the total energy and the forces on all atoms. Since the Gaussian basis sets have been used for the wave-function expansion, the correction term of the force has also been taken into account, in addition to the Hellmann-Feynman term. By performing the calculation using these pseudopotentials and the Gaussian basis sets, the lattice constant and the bulk modulus of GaAs (Ref. 14) and the structure of the arsine molecule AsH_3 (Ref. 15) are reproduced.

In the present calculation of the GaAs(100) surfaces, we have adopted the repeating slab geometry to carry out the total-energy band-structure calculation with three-dimensional periodic boundary conditions. Before describing the details of this slab model, we mention the general methodology for treating the polarized surfaces of III-V semiconductors. Kaxiras *et al.*[16] argued that the repeating slab geometry with different surfaces (the Ga-terminated surface on one side and the As-terminated surface on the other) introduces a spurious field in the vacuum region affecting the surface reconstructions. Several efforts were made to avoid this field. For example, Kaxiras *et al.*[16] imposed an artificial-inversion symmetry of the slab containing two planes of the same kind of atoms. On the other hand, Ohno and Shiraishi[17] terminated one side of the slab with fictitious H atoms to avoid charge transfer between two sides of the slab. In the present work for the GaAs(100) surface, we have terminated both sides of the slab with As layers. Contrary to the previous methods, the stoichiometry of the present slab does not correspond to that of GaAs (Ga:As=1:1). However, this discrepancy does not affect the surface structures when the thickness of the slab is large enough. We have found that a five-layer slab gives well-converged results.[18] We have also confirmed that the total energy is well converged when the vacuum region is more than four atomic layers thick.

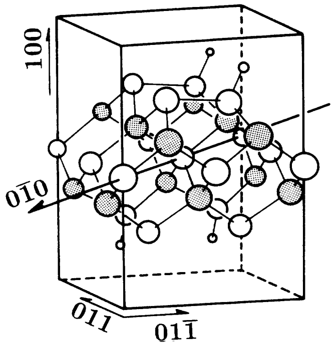

FIG. 1. The unit cell of the repeating slab geometry used in the present calculations. The open and dotted circles are As and Ga atoms, respectively. The small circles are H atoms. There is a C_2 symmetry that keeps the geometry unchanged upon a 180° rotation around the $[0\bar{1}0]$ axis.

Next, we describe details of the slab geometry. We have introduced dimerized As atoms on each side of the slab and then placed a H_2 molecule or two H atoms on each side as well. The orientations of the two surfaces on both sides of the slab make an angle of 90°, so we have introduced a 2×2 periodic lateral boundary condition in which two As dimers exist. Figure 1 shows the atomic geometry of the slab model. There is a C_2 symmetry in the system, which keeps the atomic configuration invariant upon a 180° rotation about the $[0\bar{1}0]$ axis, as is shown in Fig. 1. This symmetry reduces the calculation time but never restricts the degrees of freedom of possible atomic configurations on each surface. To perform the band-structure calculation of this slab model, the interval of meshes for the fast Fourier transformation has been set to 0.25 a.u. and three *k* points per irreducible wedge of the first Brillouin zone (eight per whole zone) of the 2×2 unit cell have been used for the momentum space integration.

In order to investigate molecular- and atomic-hydrogen reactions on the GaAs(100) surface, we have performed the geometry optimization of H atoms and surface As atoms under the C_2 symmetry until the calculated forces on H atoms and surface As atoms are less than 0.01 Ry/a.u.

III. REACTION OF MOLECULAR HYDROGEN

There have been several previous reports that H_2 molecules interact with the GaAs(100) surface. Nagata *et al.*[19] and Maruno *et al.*[20] reported that the growth rate of GaAs decreased due to the interaction between the H_2 molecules and the GaAs(100) surface. Svob, Grattepain, and Marfaing[21] presented experimental results that D_2 molecules diffused into GaAs from a gaseous source. However, there are many other reports[4,22–25] in the literature arguing that there is no experimental evidence that the H_2 molecule sits on GaAs. In order to investigate whether the H_2 molecule interacts with the GaAs(100) surface, we have calculated the total energy and the forces on the H atoms of the H_2 molecule on the surface.

We have considered two candidate sites on the GaAs(100) surface, one site on the dimer (*A*) and another between neighboring dimers (*B*). Other sites, e.g., between the dimer rows, have been ruled out, since on those sites the distance between the H_2 molecule and the surface As atoms is probably too large for any interaction to occur. On both sites, we have started the geometry optimization by locating the H_2 molecule at a height of 1.5 Å, which is about two times longer than the bond length of H_2. In order to avoid any symmetric restriction of the geometry optimization, we have located the H_2 molecule by tilting its bond axis in arbitrary orientations with respect to the surface.

First, for site *A*, we have placed the H_2 molecule with its bond axis tilted by 30°, as shown in Fig. 2(a). Because of the C_2 symmetry of the slab, two H_2 molecules have been placed at each site (*A*) on both sides of the slab. As can be seen from Fig. 2(a), the forces on the two H atoms act to desorb the H_2 molecule from the surface rather than to dissociate the molecule. (Note that the forces are not directed parallel to the bond axis of the H_2 molecule, which might be hard for readers to recognize from the view of this figure.) We have moved the H atoms according to the calculated forces toward the total-energy minimized configuration. In the course of the optimization, only the H atoms have been moved until forces on them are reduced less than 0.01 Ry/a.u. Figure 2(b) shows the optimized geometry, where the distance between the center of the H_2 molecule and that of the As dimer is 1.83 Å. The forces on the H atoms, which remain less than 0.01 Ry/a.u., are still directed away from the surface. It should be noted that the bond axis of the H_2 molecule is parallel to that of the surface As dimer. This atomic geometry has been found to be stable against the twist of the H_2 molecule on the (100) plane. The bond length of the H_2 molecule in the optimized geometry is 0.87 Å, which is slightly longer than that of the optimized bond length of the isolated H_2 molecule, 0.78 Å, obtained by a LDA calculation with the present basis set. The optimized atomic geometry and the remnant forces indicate that the H_2 molecule on the *A* site neither dissociates nor sits on the surface.

Next, on site *B*, the H_2 molecule has been placed with its bond axis rotated by 60° and 10° from the [100] and [01$\bar{1}$] directions, respectively, as shown in Fig. 3(a). Although the forces seem to dissociate the H_2 molecule in the starting geometry, the molecule is still preserved after the geometry optimization as is shown in Fig. 3(b), where the H_2 molecule center is located at 1.55 Å above the surface. The bond length of the H_2 molecule at the optimized geometry is 0.78 Å, same as that of the isolated, H_2 molecule. The remnant forces are still directed away from the surface, which indicates that the H_2 molecule neither sits on nor penetrates through the surface in the site *B*.

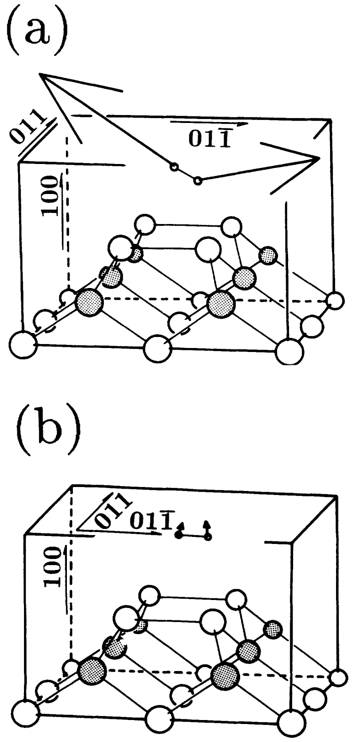

FIG. 2. A molecular hydrogen atom, the center of which is approaching directly above the rear As dimer (a) before the geometry optimization and (b) after the optimization by the total-energy and force calculations. The forces on all H atoms are shown as arrows: the maximum value is 0.173 Ry/a.u.

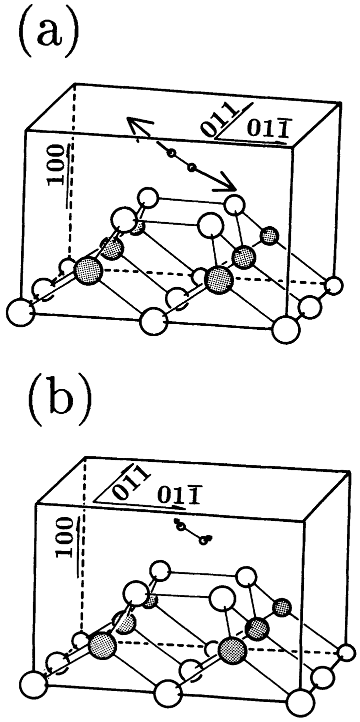

FIG. 3. A molecular hydrogen atom, the center of which is approaching between the neighboring As dimers (a) before the geometry optimization and (b) after the optimization. The forces on all H atoms are shown as arrows: the maximum value is 0.062 Ry/a.u.

We have calculated the local density of states (LDOS) for the two optimized geometries to clarify the reason for the repulsive interaction between the H_2 molecule and the surface. The LDOS peaks for the occupied and unoccupied orbitals of the H_2 differ from those of the As dimer by about 5 eV, indicating that orbital hybridizations between the H atoms and surface As atoms are hard to achieve. Consequently, it is difficult for the H_2 molecule approaching the surface to make As-H bonds.

In these calculations we could not find stable adsorption sites for H_2 on the As-terminated GaAs(100) surface. If adsorption of the H_2 molecule on the surface does occur, the adsorption sites must be away from the surface by 1.83 and 1.55 Å above the sites A and B, respectively, or be above other sites. (However, these other sites seem to us to be unlikely.) We have not obtained the activation barrier for the dissociation of the H_2 molecule. Recently, the Hartree-Fock calculation with a cluster model has been performed by Nonoyama, Aoyagi, and Namba,[26] and they report that the activation barrier for the dissociation of molecular hydrogen on the GaAs(100) surface is about 2.5 eV. We expect that adsorption of atomic hydrogen, which we will show in the next section, rarely occurs when the GaAs(100) surface is exposed to the H_2 gas.

IV. ADSORPTION OF ATOMIC HYDROGEN

In this section, we discuss the stable and metastable configurations of H and surface As atoms on the GaAs(100) surfaces. We consider two H atoms per 2×2 unit cell of the GaAs(100) surface. Hence, the coverage of H atoms corresponds to 0.5 ML. By calculating the forces, we have performed the geometry optimization of H and surface As atoms. We started the geometry optimization by setting two H atoms in the three geometries shown in Figs. 4(a)–4(c). The adsorption sites are (a) two dangling bonds of one of the two As dimers, (b) one dangling bond of each As dimer on the same side, and (c) one dangling bond of each As dimer on alternate sides. The geometries of Figs. 4(a) and 4(c) have a 2×2 periodic boundary condition, while the geometry of Fig. 4(b) has a 2×1 periodic boundary condition. However, as is mentioned before, the slab geometry used has two surfaces oriented 90° from each other. We have thus performed the calculation with the 2×2 unit cell even for the geometry of Fig. 4(b).

Figure 5(a) shows the optimized atomic configuration with the starting geometry of Fig. 4(a). Two H atoms are adsorbed on two dangling bonds of one of the two As dimers while the other non-H-activated As dimer is slightly lifted up. The As-H bond length is 1.56 Å. According to the simple electron counting model,[9] each As atom provides $\frac{5}{4}$ electrons per chemical bond, while each Ga atom provides $\frac{3}{4}$ electrons per chemical bond, and each chemical bond requires two electrons. According to this electron counting model, without the H-atom adsorption each As dimer needs one more electron to have a lone

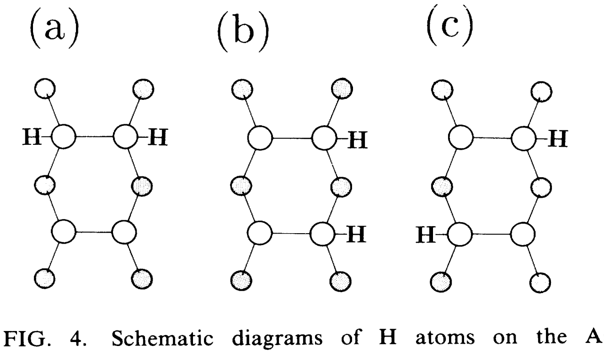

FIG. 4. Schematic diagrams of H atoms on the As-terminated GaAs(100) surface shown as top views. Dotted and open circles are Ga and As atoms, respectively. The adsorption sites for H atoms are (a) two dangling bonds of one of the two As dimers, (b) one dangling bond of each As dimer on the same side, and (c) one dangling bond of each As dimer on alternate sides.

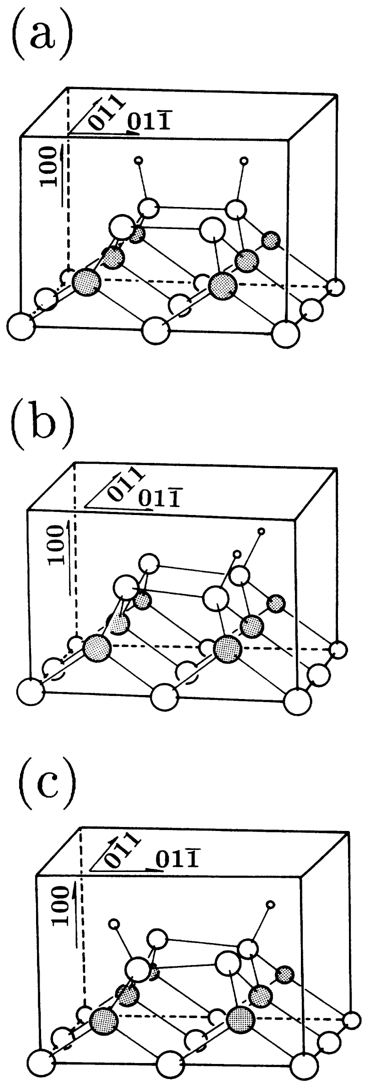

FIG. 5. Optimized atomic geometries of adsorbed H atoms: Geometries (a), (b), and (c) were obtained from the starting geometries of Figs. 4(a), 4(b), and 4(c), respectively.

pair on each of its two As sites. The H atom provides one electron so that the As dimer with two H atoms has one excess electron that is then used by the other As dimer to make a lone pair on each As site. The calculated electronic structure is nonmetallic, which is consistent with the above explanation. For the lone pairs on surface As sites, an *s*-like orbital is energetically favorable. The As atoms therefore tend to move upward because the bond angles of the black bonds become closer to 90°, allowing the lone pair orbitals to have a large *s* component. However, in this case, a higher As dimer requires a large lattice distortion, i.e., extension of the As-Ga back bonds, with an increase in the total energy. Thus the amount of the distortion is limited, and the lone pairs on surface As sites include only small-*s* components.

Figures 5(b) and 5(c) show the optimized atomic geometries calculated from the starting geometries shown in Figs. 4(b) and 4(c), respectively. In both cases, the As dimer buckles: The H-adsorbed As atom moves downward, while the other As atom moves upward. The As-H bond length is found to be 1.6 Å in both geometries. This reconstruction is also explained by the simple electron counting model. The H atom sits on one of the two As atoms of each dimer and provides one electron which is used in the As-H chemical bond. Now, the other As can have a lone pair. Indeed, the calculated electronic structure of Figs. 5(b) and 5(c) is again nonmetallic. As mentioned above, an *s*-like orbital is energetically favorable for the lone pair. On the other hand, the H-adsorbed As atom tends to have a *p* component to strengthen the As-H bond. The buckling of the dimer make this possible.[27] In contrast to the raised As dimer of Fig. 5(a), the buckling of the As dimer requires little energy for the lattice distortion because the buckling keeps the As-Ga back bond length almost unchanged. Consequently, H adsorption easily occurs and the total energy decreases. Figure 6 shows a valence charge contour map for the geometry of Fig. 5(c) in the plane which includes the As dimer and the adsorbed H atom. There is a high charge density around the As-H bond (σ bond) and a similar charge density almost spherically distributed around another As atom (*s*-like lone pair).

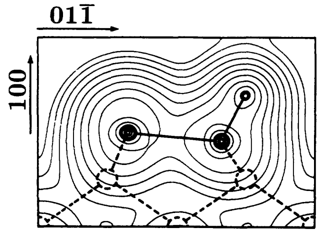

FIG. 6. A valence charge contour map in the plane containing the $[01\bar{1}]$ and [100] axes for the geometry of Fig. 5(c). One H atom (small circle) and two As atoms of the dimer are located in the plane. The dotted circles are second-layer Ga atoms and the third layer As atoms that are out of the plane. The contour lines are not in a linear sequence. Each line denotes twice the charge density of the preceding line, with a maximum charge density shown of $0.13e$ (a.u.)^3.

TABLE I. Heat of formation of the geometries of Figs. 5(a)–5(c), obtained by comparing the total energy for each of the H-adsorbed geometries with that of the 2×2 surface plus that of a H_2 molecule.

Geometry	Heat of formation (eV/H_2)
Fig. 5(a)	0.26
Fig. 5(b)	0.55
Fig. 5(c)	0.58

The heat of formation upon H adsorption in these geometries is listed in Table I in units of eV per H_2. This has been obtained by comparing the total energy for each of the H-adsorbed geometries with that of the 2×2 surface plus that of a H_2 molecule. The geometry in Fig. 5(a) has the lowest value among the three. The order of the heat of formation corresponds to the amount of *s* components in the lone pairs on surface As sites: The lone pair on each surface As site in Fig. 5(a) has the smallest *s* component among the three geometries, so that the total energy of this geometry is highest. The total energies for Figs. 5(b) and 5(c) are almost identical. If the repulsive interaction between two lone pairs on surface As sites was large, the geometry of Fig. 5(c) would be the most stable because the distance between the neighboring lone pairs on surface As sites is longer than that in Fig. 5(b).

V. TOTAL-ENERGY COMPARISON WITH THE 2×4 SURFACE

As stated previously, the most stable geometry of the As-terminated GaAs(100) surface includes three As dimers with a single missing dimer in the basic unit. In this structure, all surface As atoms have lone pairs, while all surface Ga atoms have empty dangling bonds. Such a nonmetallic electronic configuration can be explained by the simple electron counting model.[9] On the other hand, the geometries of H-adsorbed GaAs(100) surfaces discussed above also have nonmetallic electronic configurations; all surface As atoms have either lone pairs or are terminated by H atoms. The question then arises as to which of these structures is more stable. This motivated us to perform a total-energy comparison of these atomic configurations.

The stoichiometry of surface Ga and As atoms on the (100) 2×4 surface differs from that of our present (100) 2×2 surfaces. To compensate for the difference, we have introduced two AsH_3 molecules on the (100) 2×4 surface and then compared the corresponding total energy with twice the total energy of the H-adsorbed (100) 2×2 surface plus the total energy of one H_2 molecule. In our method, the total-energy calculation of the 2×4 GaAs(100) surface requires 4×4 lateral boundary conditions, since the orientations of the two surfaces of the slab are rotated 90° to each other. Such a large scale calculation is beyond our presentability. Instead of performing a total-energy calculation of the 2×4 surface, we have used our results from a recent calculation of another 2×2 unit cell, i.e., one As dimer and one missing dimer per unit cell,[28] and have combined the previous results of Ref. 29.

The total-energy comparison has been carried out as follows: According to our calculations, we obtain

$$2E_{2\times2}(2\mathrm{H})+E(\mathrm{H}_2)+2.4\ \mathrm{eV}/2\times2 = E_{2\times2}+E_{2\times2}(\mathrm{miss})+2E(\mathrm{AsH}_3)\ , \quad (1)$$

where $E_{2\times2}(2\mathrm{H})$ and $E(\mathrm{H}_2)$ are the total energies of the H-adsorbed GaAs(100) 2×2 surface and the H_2 molecule, respectively. $E_{2\times2}$ and $E_{2\times2}(\mathrm{miss})$ are the total energies of the GaAs(100) 2×2 surfaces with and without the missing As dimer, respectively. $E(\mathrm{AsH}_3)$ is the total energy of the AsH_3 molecule. Here, we have substituted the total energy of Fig. 5(b) [or 5(c)] in $E_{2\times2}(2\mathrm{H})$. Next, by referring to the previous results of Ref. 29, we obtain

$$E_{2\times4}+2.0\ \mathrm{eV}/2\times2=E_{2\times2}+E_{2\times2}(\mathrm{miss})\ , \quad (2)$$

where $E_{2\times4}$ indicates the total energy of the GaAs(100) 2×4 surface. Finally, by combining Eqs. (1) and (2), we derive that

$$2E_{2\times2}(2\mathrm{H})+E(\mathrm{H}_2)+0.4\ \mathrm{eV}/2\times2 = E_{2\times4}+2E(\mathrm{AsH}_3)\ . \quad (3)$$

Equation (3) indicates that the H-adsorbed GaAs(100) surface with one H_2 molecule is more stable than the GaAs(100) 2×4 surface with two AsH_3 molecules. However, considering the accuracy of the present calculations, the total-energy difference of 0.4 eV/2×2 is too small to conclude that the H-adsorbed surface is more stable. Furthermore, the chemical potentials of AsH_3 and H_2 molecules depend on the concentration ratio of these gases in equilibrium, so we restrict ourselves to pointing out the possibility of the appearance of the geometries of Figs. 5(b) and 5(c) under the condition of exposure of the surface to arsine and hydrogen gases.

VI. SUMMARY AND DISCUSSION

In summary, we have performed a total-energy band-structure and force calculation on the reactions of H_2 molecules and H atoms with the As-terminated GaAs(100) surface within the framework of the LDA. In the calculation, we have terminated both sides of the slab with As layers to avoid any spurious fields. This method enables us to introduce an artificial symmetry that reduces the calculation time without restricting the degrees of freedom in the geometry optimization. Although a different number of Ga and As atoms exist in our model, it does not affect the results when the thickness of the slab is five layers or more.

First, we have calculated the total energy and forces of the system consisting of the five-layer slab and two H_2 molecules in order to consider the possibility of a surface adsorption reaction. However, we were unable to find an adsorption site for H_2 on the GaAs(100) surface, even though the total energy of the GaAs(100) surface adsorbed by H atoms is lower than that of the bare surface plus H_2 molecules. These calculated results indicate that the surface adsorption reaction of H_2 molecules on the GaAs(100) surface requires a high activation energy. Thus, we conclude that the possibility of H_2 molecule adsorption is very low.

Next, we investigated the reaction of H atoms on the GaAs(100) surface with the same slab model. We introduced two H atoms per 2×2 unit cell of the As-dimerized surface and found that H-atom adsorption occurs while preserving the As dimers. The As dimers are distorted by H adsorption and the direction of the distortion is determined by the following two rules: (i) The non-H-activated As atoms have lone pairs in accordance with the simple electron counting model. (ii) Each lone pair tends to have *s*-like orbitals in order to lower the energy.

The simple electron counting model has been previously used to explain the atomic structure of GaAs surfaces. We have shown here that this model can be extended to the case of hydrogen adsorption on the GaAs(100) surface. In this case, not only the reconstruction but also the atomic distortion of the surface can be described by taking into consideration the orbital energy of the lone pairs on surface As sites. The electron counting model is based on the concept of a highly localized electron distribution in each chemical bond. If atoms with large covalent radii (e.g., heavy metals) existed on the surface, the electron counting model would not work well since the adsorbates have weakly localized valence electrons. Apparently, the compact nature of the H 1*s* wave function permits us to extend the model to H-activated GaAs(100) surfaces. We further expect that the electron counting model should work well in describing the adsorption of other light elements, such as boron, carbon, nitrogen, and oxygen.

Furthermore, we have performed a total-energy comparison of the hydrogen-adsorbed surface with the 2×4 GaAs(100) surface, in order to examine whether the hydrogen adsorbed surface should be observed experimentally. We have found that the total energy of the hydrogen-adsorbed GaAs(100) surface is comparable to that of the 2×4 bare surface when the surface is exposed to hydrogen and arsine gases. From this result, we conclude that there is a possibility that the bare 2×4 surface may coexist with the H-adsorbed surface. Furthermore, the H-adsorbed surface would be a mixture of the geometries of Figs. 5(b) and 5(c).

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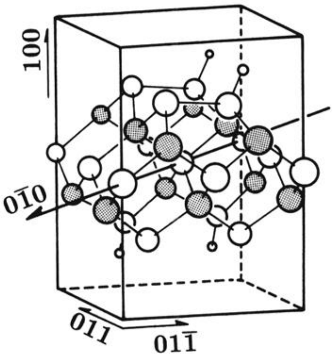

FIG. 1. The unit cell of the repeating slab geometry used in the present calculations. The open and dotted circles are As and Ga atoms, respectively. The small circles are H atoms. There is a C_2 symmetry that keeps the geometry unchanged upon a 180° rotation around the $[0\bar{1}0]$ axis.

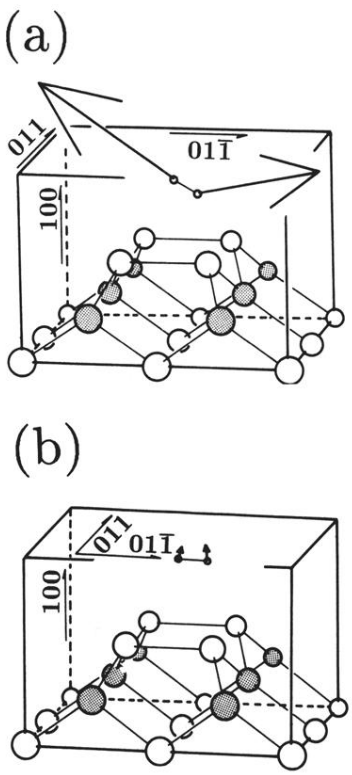

FIG. 2. A molecular hydrogen atom, the center of which is approaching directly above the rear As dimer (a) before the geometry optimization and (b) after the optimization by the total-energy and force calculations. The forces on all H atoms are shown as arrows: the maximum value is 0.173 Ry/a.u.

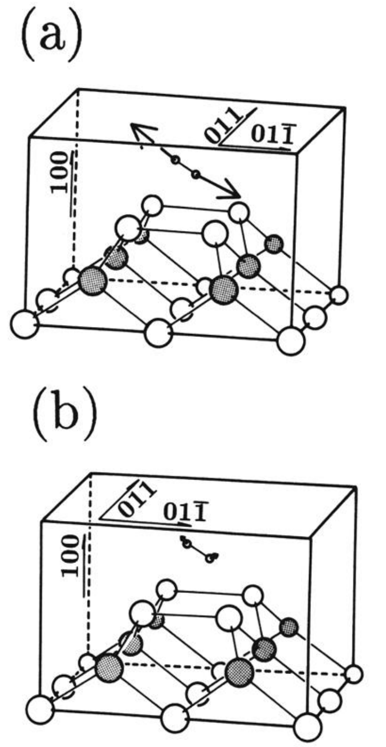

FIG. 3. A molecular hydrogen atom, the center of which is approaching between the neighboring As dimers (a) before the geometry optimization and (b) after the optimization. The forces on all H atoms are shown as arrows: the maximum value is 0.062 Ry/a.u.

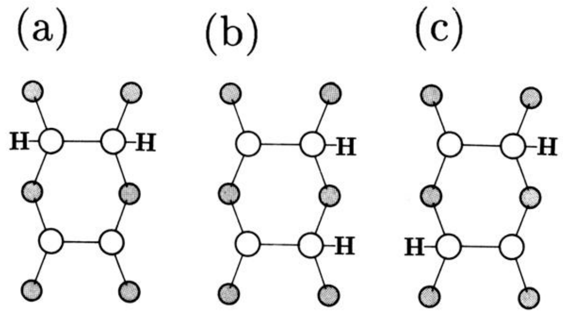

FIG. 4. Schematic diagrams of H atoms on the As-terminated GaAs(100) surface shown as top views. Dotted and open circles are Ga and As atoms, respectively. The adsorption sites for H atoms are (a) two dangling bonds of one of the two As dimers, (b) one dangling bond of each As dimer on the same side, and (c) one dangling bond of each As dimer on alternate sides.

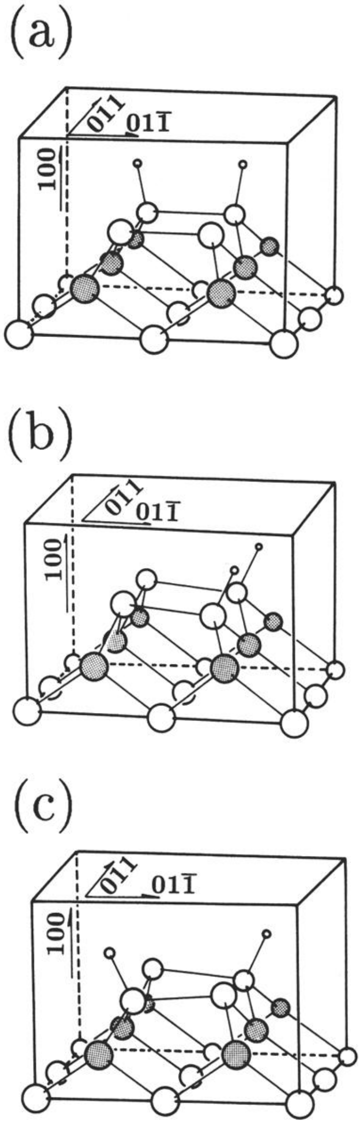

FIG. 5. Optimized atomic geometries of adsorbed H atoms: Geometries (a), (b), and (c) were obtained from the starting geometries of Figs. 4(a), 4(b), and 4(c), respectively.