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Electronic and optical properties of GaAs(001) (2 × 4) and (4 × 2) surfaces

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We present theoretical studies of the electronic and optical properties of GaAs(001) surfaces with different reconstructions at 0 K and at typical growth temperatures near 850 K. Ga-rich (4 × 2) missing-dimer surface and three different phases (α, β, and γ) of the As-rich (2 × 4) surface are considered. A nearest-neighbor tight-binding model with six orbitals (sp^3d^2) per atom is employed. Total-energy calculations are performed to determine the surface geometry for each reconstruction considered. The surface local density of states and surface dielectric functions of these surfaces are calculated. The difference between dielectric functions with [110] and [$\bar{1}$10] polarization for these surfaces is analyzed and compared to available data.

I. INTRODUCTION

Recently it has been demonstrated that the reflectance-difference spectroscopy can be used as a noninvasive real-time surface probe with monolayer sensitivity and it is equally applicable to the ultrahigh-vacuum environment of a molecular-beam-epitaxy (MBE) chamber and the atmospheric pressure environment of an organometallic chemical vapor deposition reactor.[1–5] To interpret the observed surface optical data, a theoretical analysis which relates the observed optical response to surface electronic structures has been developed recently.[6] In that work, an sp^3d^2 tight-binding model was used to calculate the dielectric functions of the (2 × 1) and (1 × 2) reconstructions of the GaAs(001) surface as an approximation to the corresponding (2 × 4) and (4 × 2) reconstructions.[6]

The (2 × 4) reconstruction for the As-rich surface and a (4 × 2) reconstruction for the Ga-rich surface is believed to be the most stable structure of GaAs(001) surfaces prepared by MBE.[7,8] Each reconstructed surface unit cell consists of three dimers formed by the surface atoms and two vacancies (or a missing dimer). Such reconstruction would balance the surface charge properly and lead to a stable surface structure. We shall refer to this structure as the "missing-dimer" structure. There are, however, other structures which would balance the surface charge and also have a (2 × 4) reconstruction. For example, the As-rich (2 × 4) reconstruction may be alternatively modeled by several different structures which account for the three different phases (α, β, and γ) observed during MBE growth.[9] The β phase which is stable at temperatures near 550 °C is most likely described by the missing-dimer structure. The α phase which is stable at higher temperatures (> 595 °C) may have two possible structures (see Fig. 3 of Ref. 9). In the first structure, the surface unit cell consists of two adjacent dimers with the other two missing. In order to balance the surface charge, the second-layer Ga atoms will also form dimers along the direction perpendicular to the top-layer As dimers. This would lead to considerable strain and appear to be energetically unfavorable. On the other hand, evidence for such a structure was found by scanning tunneling microscopy.[10] The second structure is obtained by breaking the bonds of two adjacent As dimers in the missing-dimer structure and adding one Ga dimer on top of the four As atoms. We shall call this the 2As-Ga$_2$-2As dimer-bridge structure. The γ phase which is stable at lower temperatures (≈ 470 °C) most likely has a 2As-As$_2$-2As dimer-bridge structure. This structure is just the previous 2As-Ga$_2$-2As structure with the surface Ga dimers replaced by As dimers.

In this paper we extend the theoretical analysis of Ref. 6 to treat the more complicated but realistic (2 × 4) and (4 × 2) reconstructions of the GaAs(001) surface. We shall consider the Ga-rich (4 × 2) missing-dimer structure and all three phases of the As-rich (2 × 4) reconstruction. For the α phase, we only consider the 2As-Ga$_2$-2As structure because of its simplicity. The geometry of the Ga-rich surface is depicted in Fig. 1, while the geometries of the three phases of the As-rich surface are depicted in Fig. 2. Total-energy calculations are performed to determine the positions of surface atoms in all structures considered. The surface local density of states and surface dielectric functions of these surfaces are then calculated, and results of the anisotropy of the surface dielectric functions are compared with available data.

II. THEORETICAL MODEL

Our calculations are performed in an empirical sp^3d^2 tight-binding model. Six atomic orbitals ($s, p_x, p_y, p_z, d_1, d_2$) at each atomic site are used and only nearest-neighbor interactions are included, where $d_1 \equiv d_{(x^2-y^2)/\sqrt{2}}$ and $d_2 \equiv d_{(3z^2-r^2)/\sqrt{6}}$. The d orbitals serve the same purpose as the s^* orbitals used in the popular sp^3s^* model developed by Vogl, Hjalmarson, and Dow.[11] Because of the anisotropic behavior of these two d orbitals, the sp^3d^2 model produces more realistic conduction-band structures than those obtained in the

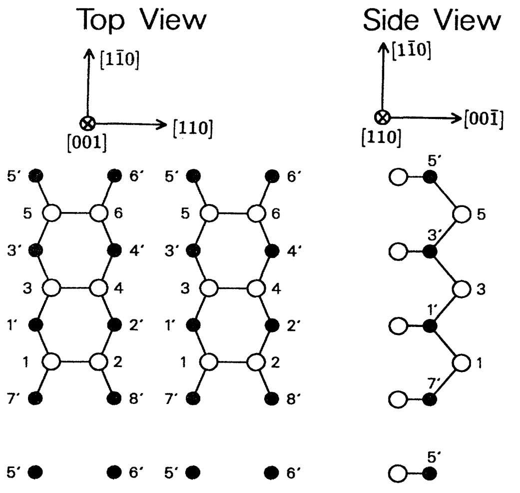

FIG. 1. Schematic diagrams of Ga-rich 4 × 2 surfaces (missing-dimer structure). Open circles denote Ga atoms and filled circles denote As atoms.

sp^3s^* model. This feature is essential to our studies of the anisotropy of the surface dielectric functions. We used two sets of interaction parameters which are appropriate for 0 K and for a typical growth temperature of 850 K, respectively. These parameters can be found in Ref. 6.

A slab method is employed to produce the surface electronic states needed in the calculation. The slab used consists of five diatomic layers of GaAs. At one end of the slab is a Ga-rich surface and at the other end is an As-rich surface. Note that when the (4 × 2) Ga-rich surface appears on the left side of the slab, it has the same surface unit cell as that of the (2 × 4) missing-dimer As-rich surface appearing on the right side of the slab. Thus, we are able to calculate the electronic properties of the (4 × 2) Ga-rich surface and the (2 × 4) As-rich surface simultaneously by using a slab with (2 × 4) surface unit cells.

Our total-energy calculation basically follows the method introduced by Chadi.[12] Details of our procedures are the same as those described in Ref. 13. We only report the total energy calculations using the 0-K tight-binding parameters. We expect and indeed find that the surface geometry determined by using the 850-K tight-binding parameters does not change appreciably. We therefore use the geometries determined at 0 K and use the 850-K parameters to calculate the electronic and optical properties of the growth surfaces. The As-As interaction parameters are taken from Ref. 14. We note that in order to determine the surface geometry at high temperatures, one should minimize the free energy instead of the total internal energy. If this is done correctly, one should be able to predict the surface geometries of the various phases at different temperatures. This is, however, beyond the scope of the present paper.

In the missing-dimer structure, the positions of the relaxed Ga (As) surface atoms are determined by keeping their ideal bond lengths and varying the two bond angles α_1 and α_2 (β_1 and β_2) as defined in Fig. 3, which illustrates the side views of different structures considered in this paper. Here the ideal bond length for each bond is taken to be the sum of the covalent radii of two atoms in the bond. The bond angles which lead to the lowest total energy are tabulated in Table I. For the Ga-rich surface,

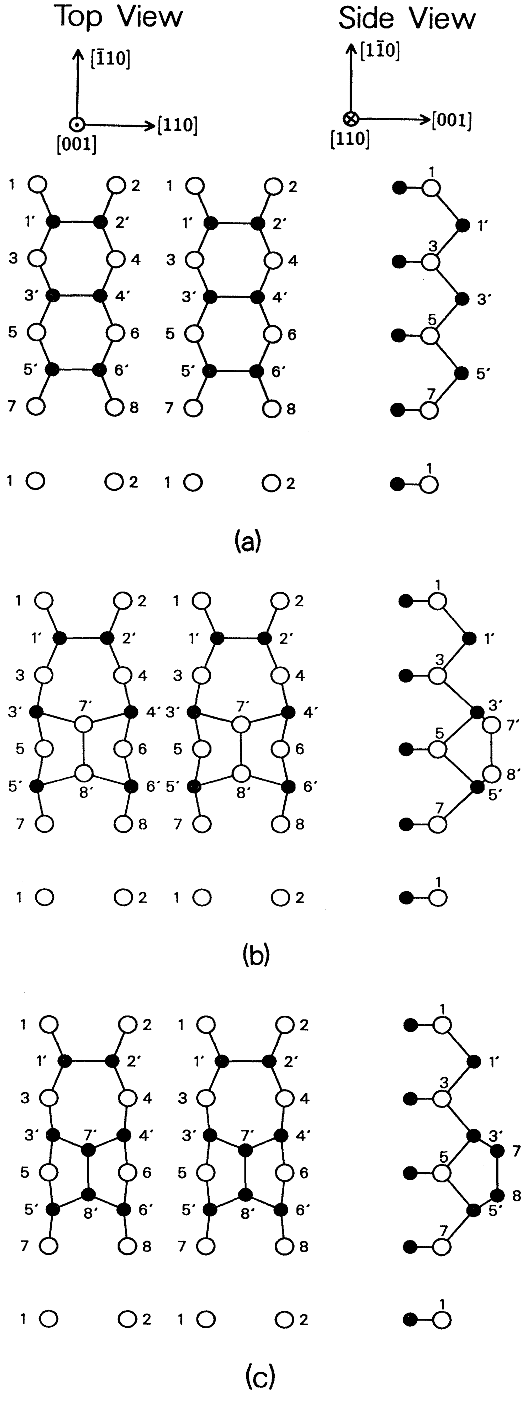

FIG. 2. Schematic diagrams of three phases of As-rich 2 × 4 surface: (a) missing-dimer structure, (b) 2As-Ga_2-2As structure, and (c) 2As-As_2-2As structure. Open circles denote Ga atoms and filled circles denote As atoms.

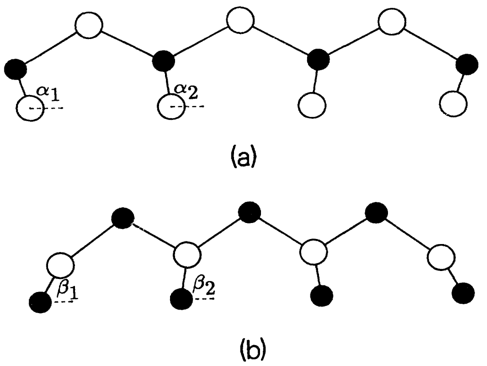

FIG. 3. Side views of Ga-rich 4×2 and As-rich 2×4 surfaces: (a) Ga missing-dimer structure, (b) As missing-dimer structure. Open circles denote Ga atoms and filled circles denote As atoms.

the dimers tend to move downward and toward the vacancy whereas for the As-rich surface, the dimers tend to move upward and away from the vacancy. This is consistent with the fact that the threefold bonded surface Ga atoms tends to form sp^2 bonding, while the threefold bonded surface As atoms tend to form p^3 bonding, leaving an occupied s-like lone pair.

In the calculations of Ref. 6, the atomic positions in the (2×1) reconstruction are taken to be the same as those predicted by self-consistent pseudopotential calculations.[15] We also performed calculations for the (2×1) reconstruction but with the positions of the surface atoms decided by the ideal bond lengths. There is no qualitative difference between the two results. This leads to the conclusion that the effects of the bond-length relaxation is much smaller than the effects of the bond rotations in surface relaxation. In order to demonstrate the effects of surface relaxation, we have also considered a nonrelaxed missing-dimer structure in which the atomic positions in the (2×4) reconstruction are kept the same as those in the (2×1) reconstruction except one surface dimer is removed in each (2×4) surface unit cell. We found that the differences in the electronic structures for relaxed and unrelaxed missing-dimer structures do not lead to substantial changes in the surface dielectric anisotropy (SDA) spectra.

In the 2As-Ga$_2$-2As and 2As-As$_2$-2As dimer-bridge structures, one extra Ga or As dimer is mounted on the top of two As dimers, and the positions of surface atoms are decided by minimizing the total energy. It is expected that the surface atoms next to the vacancy site relax similar to those in the missing-dimer structure. For simplicity, we first ignore the relaxation of the second-layer surface atoms (labeled 1–8 in Fig. 2). We then allow the surface atoms labeled 3′, 4′, 5′, and 6′ in Figs. 2(a) and 2(c) to move sideways by rotating the bonds and keeping the bond lengths the same as their ideal lengths. We assume that lateral displacements of the projections of these atoms in the (001) plane (δx) to be symmetric about the line connecting the two dimer-bridge atoms. The optimized values of δx are listed in Table I. Next, bond angles labeled β_1 and β_2 are allowed to change, and for simplicity we assume they take on the same values as those for the As-rich missing-dimer structure (as given in Table I). For the surface structure with minimum total energy we found no mid-gap surface states, indicating that the removal of mid-gap surface states tends to stabilize the surface.

TABLE I. Relaxation parameters α_1 (or β_1), α_2 (or β_2), and δx for the four geometries considered.

	(4×2)	$(2 \times 4)\beta$	$(2 \times 4)\alpha$	$(2 \times 4)\gamma$
α_1 (or β_1)	103.23°	67.88°	67.88°	67.88°
α_2 (or β_2)	90.31°	86.06°	86.06°	86.06°
δx (Å)	0.7394	0.8093	−0.2740	0.6498

By counting the number of electrons from surface atoms, we determined the Fermi level of the surface to be in the fundamental gap. Thus, all surfaces considered here are nonmetallic and all As lone-pair states are filled and all Ga dangling-bond states are empty.

III. ELECTRONIC STATES

Figure 4 shows the surface Brillouin zone (SBZ) of a (2×4) reconstruction of a GaAs (001) surface (shaded area), where the large open square is the SBZ of a (1×1) (001) surface, and the slashed area is the SBZ of a (2×1) (001) surface. The three circles (filled or empty) indicate the special points at which the electronic states are calculated and summed. The weight of the filled circle is $\frac{1}{2}$, and the weight of each empty circle is $\frac{1}{4}$. The special points are chosen in such a way that the $x + y$ direction and $x - y$ direction are equally weighted. This is an important consideration, because later on we will calculate the dielectric functions of the slab for polarization along [110] and [1$\bar{1}$0] directions and calculate their difference. Since the bulk contributions are the same for [110] and

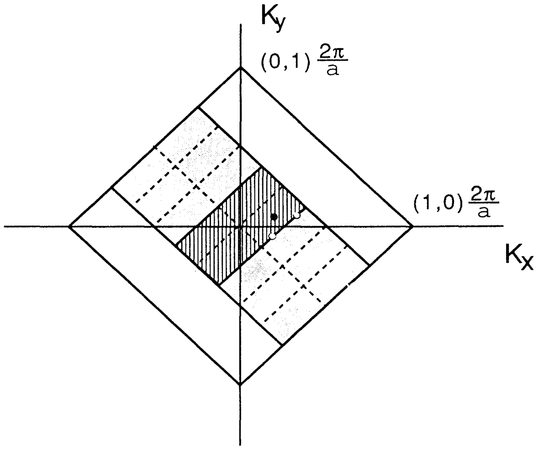

FIG. 4. Surface Brillouin zone (SBZ) for the (2×4) reconstruction of GaAs (001) surface (shaded area). The slashed area is the Brillouin zone of a (2×1) surface, and the large open square is the Brillouin zone of a (1×1) surface. The three circles denote the special points at which the optical response was calculated and summed.

$[1\bar{1}0]$ polarizations, they are canceled out in the dielectric function difference. The choice of the special points given above can avoid introducing artificial dielectric function difference due to different weighting on bulk states.

Of primary interest here are the surface states associated with dimers and dimer-bridge atoms. Their characters are best described by the local density of states. Figure 5 shows the LDOS for surface atoms in the Ga-rich (4×2) reconstruction with (a) unrelaxed and (b) relaxed missing-dimer structure. Figure 6 shows the LDOS for surface atoms in the As-rich (2×4) reconstruction with (a) unrelaxed and (b) relaxed missing-dimer structure. Figures 7 and 8 show the LDOS for surface atoms in the two 2As-Ga$_2$-2As and 2As-As$_2$-2As dimer-bridge structures of As-rich (2×4) reconstruction at 850 K with geometries described in Fig. 2. In each of these figures, the curves are marked with numbers which match the labels of surface atoms as shown in Figs. 1 and 2. We only present results for nonequivalent surface atoms. The surface atoms which are related to one another by point-group symmetry operations are considered equivalent, and the local densities of states for them are the same. The contributions from various types of surface states are marked by d, l, and b, standing for occupied dimer, lone-pair (dangling-bond), and back-bond states, respectively. The unoccupied surface states are accordingly marked by d^*, l^*, and b^*, respectively. These assignments are obtained by examining the orbital-resolved local density of states.

For the Ga-rich reconstruction with unrelaxed missing-dimer geometry, the surface states of interest include [Fig. 5(a)] (a) the occupied dimer states (labeled d) with energies in the range from -0.5 to -1.5 eV, (b) the occupied lone-pair states associated with the second-layer As atoms which are exposed [labeled As(l)] (with energies near -1 eV), (c) the unoccupied dangling-bond states (labeled l^*) with energies near 1.5 eV, (d) the unoccupied dimer states (labeled d^*) with energies near 3.5 eV, and (e) back-bond states (labeled b and b^*). The optical transitions between these occupied and unoccupied surface states would lead to either positive or negative contributions to the SDA spectra, depending on the orientations of bonds. For example, the d-l^* and d-d^* contributions are positive while the b-l^*, b-b^*, and As(l)-b^* contributions are negative. The As(l)-b^* contribution is unique to the Ga (4×2) reconstruction and was not considered in the previous calculations performed for the Ga (1×2) reconstruction.[6] Thus, we expect the SDA spectrum of the unrelaxed missing-dimer geometry to be somewhat different from that of the (1×2) reconstruction consid-

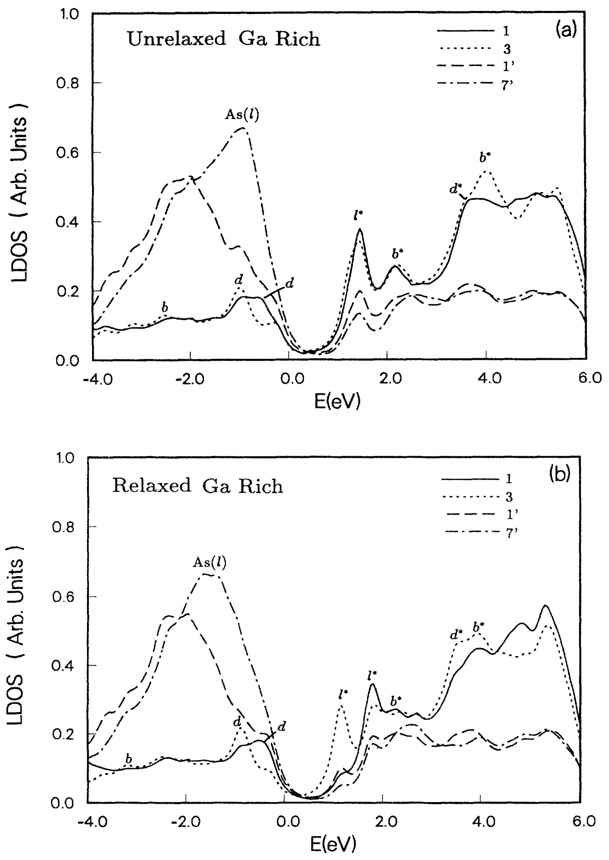

FIG. 5. Local density of states (LDOS) of the (4×2) Ga-rich surface with missing-dimer structure. (a) Unrelaxed. (b) Relaxed.

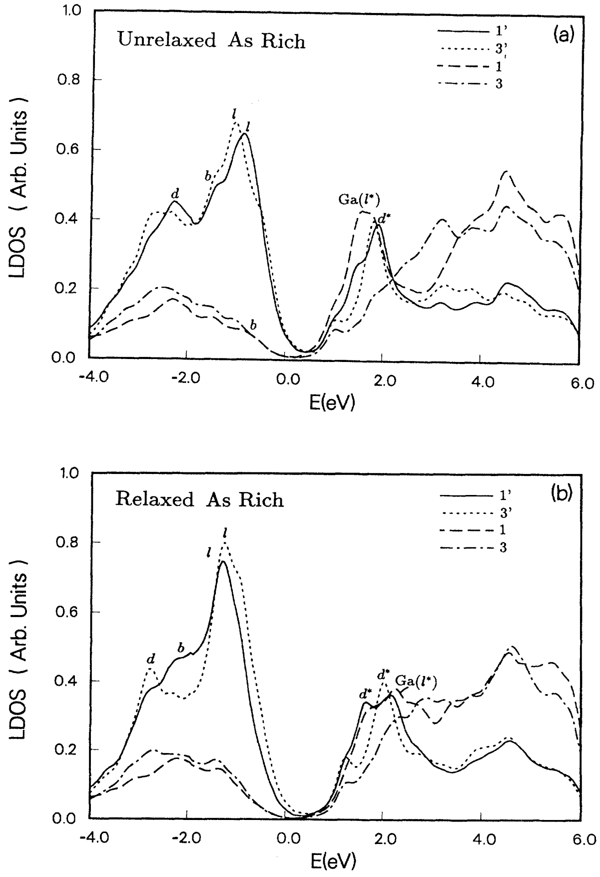

FIG. 6. Local density of states (LDOS) of the (2×4) As-rich surface with missing-dimer structure (β phase) at 850 K. (a) Unrelaxed. (b) Relaxed.

ered in Ref. 6.

For the Ga-rich reconstruction with relaxed missing-dimer geometry [Fig. 5(b)], the electronic structures are different from those for the unrelaxed missing-dimer structure in that the unoccupied dangling-bond states (l^*) for the Ga atoms next to the vacancies are pushed higher in energy by about 0.5 eV and the As(l) states are shifted downward by about 0.5 eV.

For the As-rich reconstruction with unrelaxed missing-dimer geometry, the surface states of interest include [Fig. 6(a)] (a) the occupied dimer states (labeled d) with energies near -2.5 eV, (b) the occupied lone-pair states (labeled l) with energies near -1.0 eV, (c) the unoccupied dangling-bond states associated with the second-layer Ga atoms which are exposed, [labeled Ga(l^*)] (with energies near 1.5 eV), (d) the unoccupied dimer states (labeled d^*) with energies near 2.0 eV, and (e) back-bond states (labeled b and b^*).

For the As-rich reconstruction with relaxed missing-dimer geometry [Fig. 6(b)], the electronic structures are different from those for the unrelaxed missing dimer structure in that the Ga(l^*) states are pushed higher in energy by an average of about 0.3 eV and the l states associated with atom $1'$ shifted downward by about 0.5 eV.

The 2As-Ga$_2$-2As and 2As-As$_2$-2As dimer-bridge structures have similar surface states, namely the As dimer states (d and d^*), As lone-pair states (l), Ga dimer states (for 2As-Ga$_2$-2As structure), the dangling-bond states associated with the surface Ga atoms which are exposed [Ga(l^*)], and back-bond states (b and b^*). However, the bond directions and optical transitions between surface states are different, and they lead to different SDA spectra. For the 2As-As$_2$-2As structure, there are four As—As bonds in addition to the two in As dimers. The bonding and antibonding states of these bonds are labeled $\bar{b}$ and $\bar{b}^*$, respectively, in order to be distinguished from the Ga-As back-bond states (labeled b and b^*). These states also give significant contributions to the SDA spectrum.

IV. SURFACE DIELECTRIC FUNCTIONS

We calculated the dielectric functions of GaAs slabs in the sp^3d^2 tight-binding model by using the optical matrix elements listed in Table II. The physical meaning and the determination of these elements are discussed in detail in Ref. 6. The set of parameters used here is improved from that used in Ref. 6 by adding one more

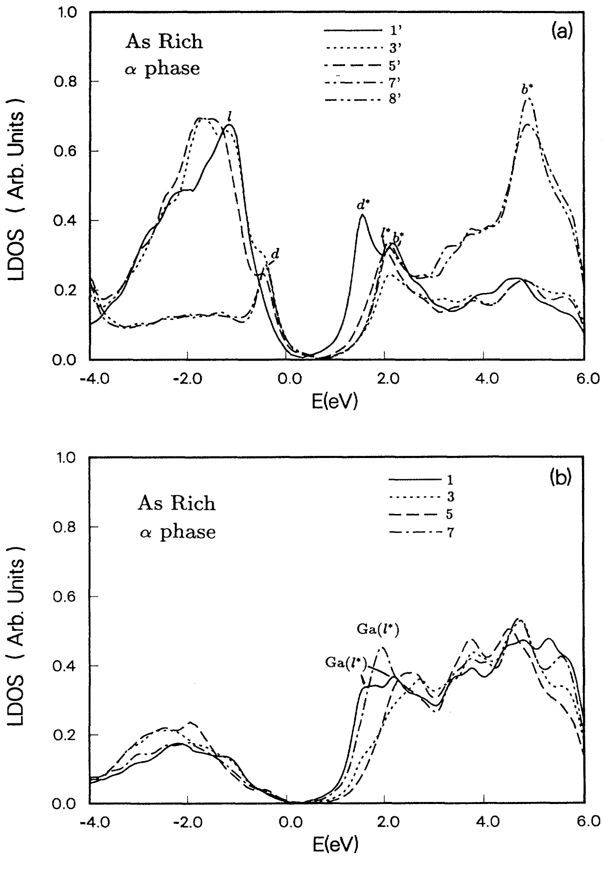

FIG. 7. Local density of states (LDOS) of the (2 × 4) As-rich surface with 2As-Ga$_2$-2As structure (α phase). (a) Top-layer atoms including the dimer-bridge atoms. (b) Second-layer atoms.

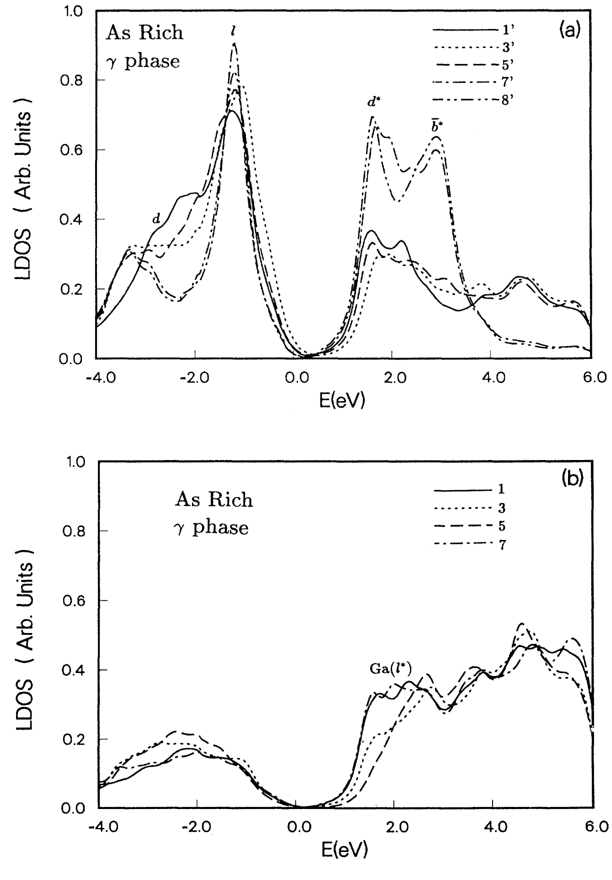

FIG. 8. Local density of states (LDOS) of the (2 × 4) As-rich surface with 2As-As$_2$-2As structure (γ phase). (a) Top-layer atoms including the dimer-bridge atoms. (b) Second-layer atoms.

TABLE II. Parameters for GaAs optical matrix elements in unit of $(\mathrm{eV})^{1/2}$.

P_{aa}	P_{cc}	P_{ss}	P_{sp_x}	$P_{p_x s}$	$P_{p_x p_x}$	P'_{aa}	P'_{cc}	P_{pd}	P_{dp}	$P_{pp\pi}$
4.073 50	3.059 53	0.387 00	−0.105 98	0.545 04	−0.738 73	0.106 31	0.264 55	0.895 52	−0.378 00	0.11178

parameter $P_{pp\pi}$ and by fitting optical matrix elements for transitions from the top three valence bands to the lowest four conduction bands to the results obtained by an empirical pseudopotential model (EPM). In Ref. 6, only optical transitions to the lowest two conduction bands are included in the fit; therefore, the spectra in the high-energy range (> 4 eV) was not described adequately. As we shall show below, with this new set of parameters, the high-energy peak structure in the SDA spectra of As-rich surfaces is much reduced and in better agreement with data. The squared optical matrix elements (P^2) obtained in the present model are shown in Fig. 9 in conjunction with the results obtained from the EPM calculation.

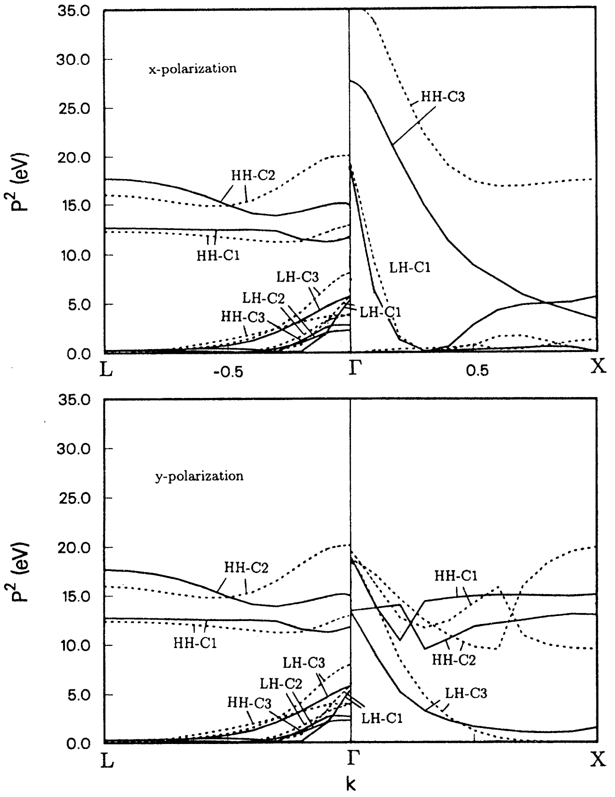

FIG. 9. Squared optical matrix elements as functions of wave vector (k) for bulk GaAs. Top: polarization along $\hat{\mathbf{x}}$. Bottom: polarization along $\hat{\mathbf{y}}$. Solid curves: EPM results. Dashed curves: present model. HH denotes the sum of two degenerate heavy-hole bands, LH denotes the light-hole band, $C1$ denotes the lowest conduction band, $C2$ denotes the second conduction band for $\mathbf{k}$ from Γ to X or the second plus third conduction bands for $\mathbf{k}$ from L to Γ, and $C3$ denotes the third plus fourth conduction bands for $\mathbf{k}$ from Γ to X or the fourth conduction band for $\mathbf{k}$ from L to Γ.

The optical properties of the slab are determined by the dielectric function $\epsilon \equiv \epsilon_1 + i\epsilon_2$. To obtain the surface contribution to the dielectric function, it is more meaningful to evaluate the product $\epsilon_2 d$. It can be shown that the surface contributions to this quantity are independent of the thickness of the slab (d) since the number of surface states is unchanged, whereas the bulk contributions grow with increasing d since the number of bulklike slab states increases. If we take the difference between $\epsilon_2([110])$ (along the dimer bonds) and $\epsilon_2([1\bar{1}0])$ (perpendicular to the dimer bonds), then the bulk contribution drops out. We denote the difference $\epsilon_2([110]) - \epsilon_2([1\bar{1}0])$ by $\Delta\epsilon_2$. It is easily seen that $\Delta\epsilon_2 d$ for the slab is just the sum of $\Delta\epsilon_2 d_s$ for the surfaces on both ends of the slab with d_s representing the effective surface layer thickness. We find that a slab of five bilayers is sufficient to decouple the contributions from the two surfaces. To identify the contribution to $\Delta\epsilon_2 d_s$ from each surface, we simply introduce a cutoff function in Eq. (1). The cutoff function has a value one for atomic orbitals located within five atomic layers from the surface, 0.5 for the bonds connecting atoms in the fifth layer and atoms in the sixth layer, and zero otherwise. The inclusion of half contributions from the bonds before truncation would adequately model the optical response of a semi-infinite slab. This is explained as follows. The incident radiation has a long penetration depth, λ (about 100–1000 Å). For a semi-infinite slab, the optical anisotropy response (S) is approximately given by

$$S = S_s + \sum_n e^{-na'/\lambda} S_n ,$$

where n labels the layer, a' is the interlayer separation, S_s is the contribution from optical transitions within orbitals located at the same site, which is appreciable only for the atoms near the surface, and S_n denotes the contribution from bonds connecting atoms in the nth layer and the $(n+1)$th layer. Since the orientation of bonds (only consider the projection in the plane) rotates 90° from one layer to another, we obtain the following relation for bonds away from the surface (i.e., bulklike bonds):

$$S_n = -S_{n+1} \text{ for } n \geq 5 .$$

Performing the sum for $n \geq 5$ and use $\lambda \gg 5a'$, we obtain

$$\sum_{n \geq 5} e^{-na'/\lambda} S_n = e^{-5a'/\lambda} S_5 / (1 + e^{-a'/\lambda}) \approx S_5/2 .$$

Figure 10 shows the calculated surface dielectric anisotropy (SDA) spectra ($\Delta\epsilon_2 d_s$ versus photon energy) of a GaAs slab with both Ga- and As-rich surfaces modeled by (a) unrelaxed missing-dimer structure and (b) relaxed missing-dimer structure. The solid and dotted curves represent contributions from the Ga- and As-rich surfaces, respectively. The dashed curve gives the net dielectric function anisotropy of the slab.

From this figure we see that the As-rich surface has much stronger dielectric anisotropy than the Ga-rich surface when they both have the missing-dimer structure. This is because the As-rich surface has much larger local density of states near the top of valence band than the Ga-rich surface (see Figs. 5 and 6) and the local densities of states near the bottom of conduction band for these two surfaces are comparable, and this leads to stronger contributions from the As-rich surface to the optical transitions in the energy range of interest.

Comparing Fig. 10(a) with Fig. 9 of Ref. 6 we see that the main features of surface dielectric anisotropy of the (2×4) reconstruction in the missing-dimer structure are qualitatively similar to those of the (2×1) reconstruction, but the relative strength for As atoms versus Ga atoms is much reduced. The physical origins of the peak structures are still the same as described in Ref. 6. The difference is mostly caused by the use of a new set of parameters for the optical matrix elements. The main effect of introducing the missing dimer is to reduce the overall strength by about 75% compared to the (2×1) calculation. For the Ga-rich missing-dimer structure, there is a dip structure labeled As(l)-b^* (near 2.1 eV) which is not present in the SDA spectrum calculated for the (2×1) reconstruction.[6] This is attributed to the transition from the occupied lone-pair states [labeled As(l)] associated with the second-layer As atoms, which are exposed as a result of the removal of Ga dimers in going from the (1×2) reconstruction to the (4×2) reconstruction, to the unoccupied back-bond states. Note that the removal of As dimers in going from the (2×1) reconstruction to the (2×4) reconstruction also leads to exposed second-layer Ga atoms. The unoccupied dangling-bond states associated with these Ga atoms [labeled Ga(l^*)] introduce contributions to the SDA spectrum at photon energies near 1.2 eV [due to the b-Ga(l^*) transition].

For the relaxed missing-dimer structures, the prominent features in the SDA spectra (due to d-l^*, l-d^*, and d-d^*) remain similar. However, the minor features due to As(l)-b^* and b-Ga(l^*) are modified (they both shift up in energy by about 0.3–0.5 eV). This is intimately related to the energy shifts of As(l) and Ga(l^*) as a result of relaxation (see discussions for Figs. 5 and 6).

In Fig. 11 we compare the calculated SDA spectra for As-rich surface with three different (2×4) reconstructions (α, β, and γ phases). Even in the 2As-As$_2$-2As structure (γ phase), there are substantial SDA signal between 4 and 5 eV. One might naively expect that in the 2As-As$_2$-2As structure, there is one As dimer along the [110] direction and one along the $[1\bar{1}0]$ direction and the dielectric function anisotropy associated with dimers should be canceled. The realistic situation, however, is much more complicated. The optical transitions form occupied to unoccupied dimers are indeed nearly canceled, however, other contributions set in. Note that all the top-layer As atoms [labeled 1′-8′ in Fig. 2(c)] have occupied lone-pair states and there exist four As—As bonds in addition to the two As dimer bonds [see Fig. 2(c)]. The optical transitions from these lone-pair states to the nearby As-As antibonding states (labeled $\bar{b}^*$) lead to substantial con-

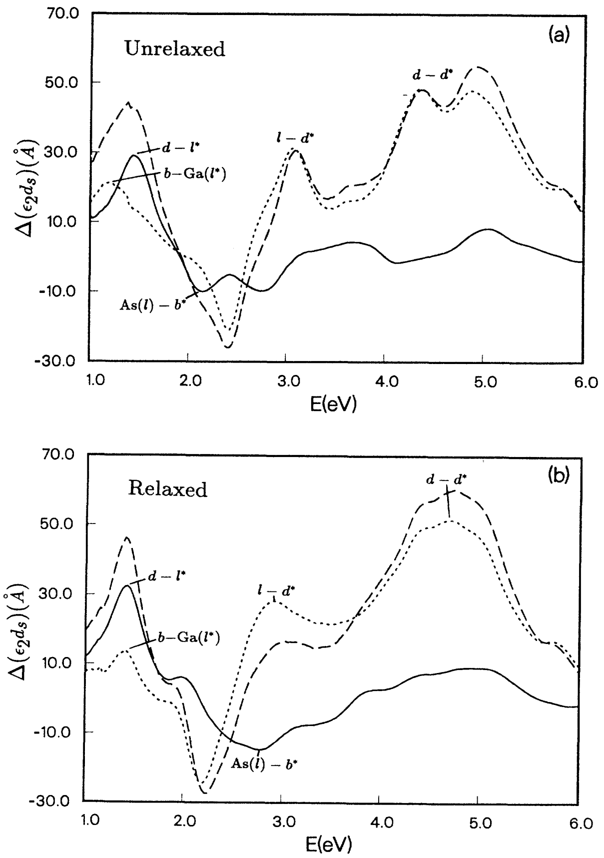

FIG. 10. Dielectric anisotropy spectra ($\Delta\epsilon_2 d_s$) of the GaAs slab with both Ga- and As-rich surfaces with the missing-dimer structure. The solid and dotted curves are contributions from the Ga- and As-rich surfaces, respectively, and the dashed curve is the total. (a) Unrelaxed, (b) relaxed.

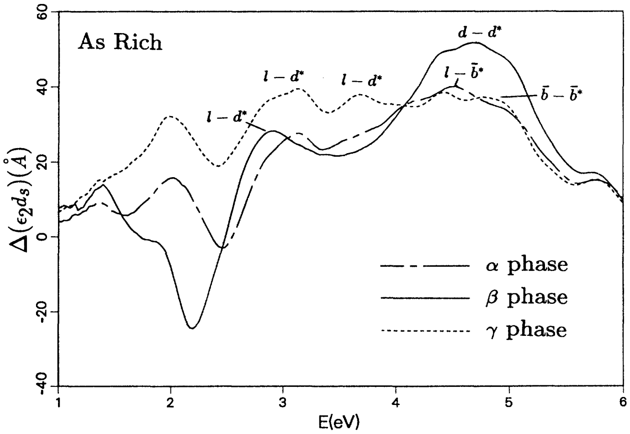

FIG. 11. Comparison among the calculated surface dielectric anisotropy (SDA) spectra for three different As-rich 2×4 reconstructions. Solid curve: relaxed missing-dimer structure (β phase). Dash-dotted curve: 2As-Ga$_2$-2As structure (α phase). Dotted curve: 2As-As$_2$-2As structure (γ phase).

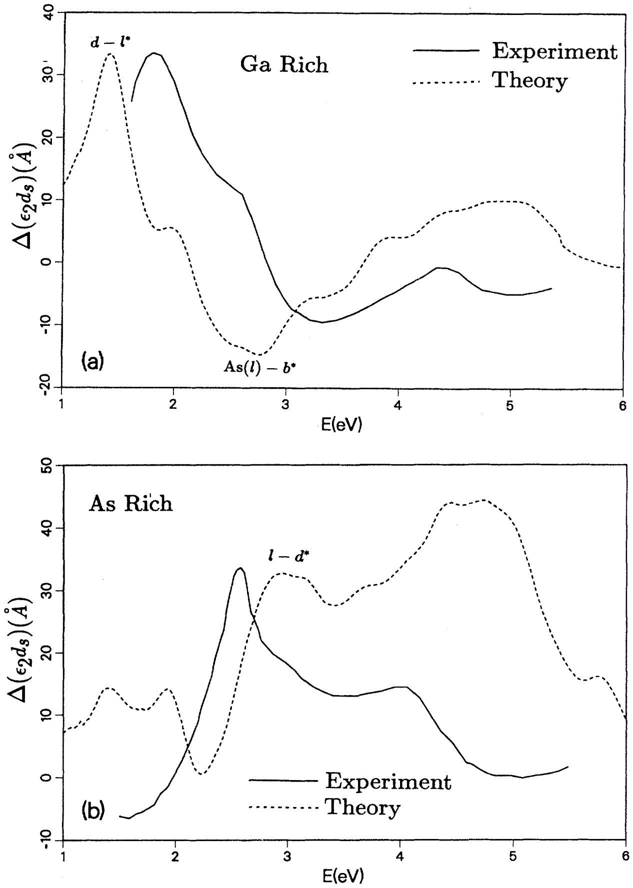

FIG. 12. Comparison between the calculated surface dielectric anisotropy (SDA) spectra and the measured SDA data. (a) Ga-rich 4 × 2 reconstruction. (b) As-rich 2 × 4 reconstruction at 510 °C. Data are taken from Ref. 5.

tributions to the SDA spectra at photon energies near 4.5 eV. The bonding to antibonding transitions for these additional As—As bonds lead to a positive contribution in the SDA spectrum near 5 eV (marked $\bar{b}$-$\bar{b}^*$). For similar reason the 2As-Ga$_2$-2As structure also shows strong positive contributions in the SDA spectra near 4–5 eV. The d-d^* contribution is still present for the only As dimer existing.

Figure 12(a) shows the comparison between the calculated SDA spectrum for the Ga-rich surface with the relaxed missing-dimer structure (dashed curve) and the measured SDA data for the corresponding GaAs (4 × 2) surface (solid curve).[5] We find that our theoretical results seem to track the data reasonably well, except for a rigid shift by about 0.5 eV. Such an energy difference is of the same size as the uncertainty of the present tight-binding model in terms of predicting energy positions of surface states.

Figure 12(b) shows the comparison between the measured SDA data for the GaAs (2 × 4) surface at 510 °C (Ref. 5) and the average of the calculated SDA spectra for As-rich surface with both missing-dimer and dimer-bridge geometries. The SDA spectra were measured for the As-rich (2 × 4) reconstruction that occurs at 510 °C during interrupted growth by MBE. This temperature is between the two temperatures at which the β and γ phases are observed. Thus, we expect the surface to have admixture of both missing-dimer and 2As-As$_2$-2As structures. The theoretical prediction for the l-d^* transition accounts for the main peak (near 2.5 eV) in the experiment. However, the shoulder structure observed near 4 eV is about a factor of 2 smaller than the predicted peak structure due to d-d^* (in the β phase) and l-$\bar{b}^*$ (in the γ phase) transitions.

In the present calculations, we have ignored the excitonic and local-field effect.[16,17] Such effects, if included, would enhance the low-energy part while reducing the high-energy part of the dielectric function and it would account for part of the discrepancy between the theory and experiment.

V. SUMMARY

We have presented a tight-binding calculation of the dielectric functions of the (001) surfaces of a GaAs slab. Ga-rich surface with (4 × 2) missing dimer reconstruction and As-rich (2 × 4) surface with three different atomic geometries (missing dimer, 2As-Ga$_2$-2As, and 2As-As$_2$-2As structures) are considered. The surface structure of the reconstruction are calculated by the minimization of total energy. We have studied the band structures, surface local density of states, and surface dielectric functions of these surfaces. The dielectric anisotropy for these surfaces are analyzed and compared with the available data. We obtain fairly good agreement between theory and experiment for the Ga-rich surface, but not as good for the As-rich surfaces. We feel that the realistic As-rich surfaces are more complicated than the structures considered in the present calculation, and further research is needed to resolve this issue.

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