Optical anisotropy of the GaAs(001) surface

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The anisotropic optical response of (2×4) As-terminated and (4×2) Ga-terminated β and $\beta2$ GaAs(001) surfaces is studied by using first-principles nonlocal pseudopotentials in a density-functional-theory framework within the local-density approximation. The calculated surface dielectric function anisotropy agrees well with reflectance-difference spectroscopy experiments for the As-terminated $\beta2$ surface and for the Ga-terminated β and $\beta2$ surfaces. Most of the calculated anisotropy comes from transitions involving only subsurface, bulklike electronic states that are perturbed by the surface; states confined at the surface, including those localized at the surface dimers, contribute little to the anisotropy. [S0163-1829(97)01240-X]

Real-time monitoring of surfaces during growth and etching, noninvasively and independent of the process environment, has spurred the recent interest in developing surface-sensitive optical probes.[1-3] In surface photoabsorption (SPA) spectroscopy,[1] the reflectance of p-polarized light incident near the pseudo-Brewster angle is monitored during a cyclic process, such as atomic layer epitaxy, which effectively tracks the variation in the surface dielectric function with time. In reflectance difference spectroscopy (RDS),[2] the difference in the reflectance of normally incident light with orthogonal polarizations is monitored; the reduced symmetry of the surface relative to the bulk leads to an anisotropy in the optical dielectric function associated with the surface. To exploit these techniques fully, the origin of the surface-specific response must be determined. In this paper, the anisotropic response of the Ga(001) surface is calculated, and the electronic transitions responsible for the RDS signal are identified.

The GaAs(001) surface exhibits several reconstructions, depending on preparation history and surface stoichiometry, ranging from the As-rich $c(4\times4)$ structure to the Ga-rich $c(8\times2)$ reconstruction. Among them, the As-rich (2×4) surface is of the most technological interest, since molecular-beam epitaxy (MBE) usually starts and ends with this surface. The most widely accepted picture of this surface is the so-called missing dimer structure, in which surface arsenic atoms dimerize along the $[\bar{1}10]$ direction (leading to the 2 × symmetry), with every fourth dimer missing along the $[110]$ direction (leading to the ×4 symmetry) $[(2\times4)\text{-}\beta]$.[4] However, recent scanning tunneling microscopy and first-principles calculations[4,5] seem to favor a surface with two topmost As dimers, a missing second-layer Ga pair, and a third-layer As dimer $[(2\times4)\text{-}\beta2]$. The Ga-rich (4×2) surface also has β and $\beta2$ versions.

It has been more difficult to determine the origin of the anisotropic surface optical response in GaAs than for Si,[6] in part because the main features of the GaAs surface optical anisotropy are near the interband critical points. This anisotropy has been attributed to local-field effects,[7] the electro-optic effect,[8] reconstruction,[9] surface dislocations,[10] and surface roughness.[11]

Chang, Ren, and Aspnes[9] calculated the optical anisotropy of As- and Ga-terminated GaAs(001) surfaces

$[(2\times4)\text{-}(\alpha,\beta,\gamma)$ and $(4\times2)]$ by using a tight-binding model, and assigned the observed RDS peaks to electronic transitions localized at the As and Ga dimers on the surface. They obtained fairly good agreement with experiments for Ga-rich surfaces, but relatively poor agreement for As-rich surfaces, which suggested that the surface structure assumed for the As-termination might have been incorrect. The recent *ab initio* pseudopotential calculations of three alternative (and fixed) structures of the As-terminated GaAs(001) surface by Morris and co-workers:[12,13] [which did not include the $(4\times2)\text{-}\beta2$ structure], showed that calculated RDS spectra depend critically on atom positions, including the second-layer relaxations. In this paper, we report density-functional-theory (DFT)–local-density-approximation (LDA) calculations in which the atomic structure is optimized before determining the optical response of the β and $\beta2$ versions of the (2×4) and (4×2) GaAs(001) surfaces.

The atomic and electronic structure of the surfaces are determined in the DFT framework within the LDA. The ion-electron interactions are treated with general norm-conserving pseudopotentials[14] in the fully separable form suggested by Kleinman and Bylander.[15,16] The surface is modeled with a supercell of eight layers of Ga and As planes, and five bulk equivalent layers of vacuum in the surface perpendicular direction. Noninteresting surfaces are terminated with pseudohydrogens.[17] A plane-wave basis set is used for the expansion of electronic wave functions. The kinetic-energy cutoff of the basis set is 12 Ry. Brillouin-zone integrations are performed using four special **k** points that are chosen to prevent artificial optical anisotropy.[9,18] (See also Refs. 19 and 20.) This standard supercell size, number of special **k** points, and basis set cutoff were checked for convergence by analyzing the As-terminated $(2\times4)\text{-}\beta$ surface using an eight special **k**-point set, a 14-atomic-layer supercell, and a 15-Ry basis set cutoff. There were no appreciable differences in the calculated quantities using these or the standard parameters. This convergence is assumed to hold for all the other surfaces that are analyzed here.

The atomic and electronic structure of the surface are determined in an integrated iterative approach, similar to the Car-Parinello method, by starting from a bulk-terminated surface, solving the Kohn-Sham equations, and calculating the Hellmann-Feynman forces on the atoms—and then mov-

ing them to minimize these forces. The force convergence limit is 5 meV/Å. The obtained electronic wave functions and energies are used to calculate the surface dielectric function as outlined by Manghi *et al.*[19] The "band gap" problem of DFT-LDA and its effect on the dielectric function are partially corrected with the simple scissor operator scheme,[21] which amounts to shifting the conduction bands up by a constant value Δ (0.8 eV) independent of the **k** vector. The resulting reconstructions are very similar to those determined in Ref. 5 (Ref. 22, see also Refs. 23 and 24).

Some of the features of the β and $\beta 2$ reconstructions of the Ga- and As-terminated surfaces calculated here are similar to the relaxation of anions and cations on GaAs(110), and can be explained by considering charge-transfer effects and the bond angles in small molecules containing Ga or As. Since the dangling-bond level of Ga is higher in energy than that of As, there is electron transfer from Ga to As dangling bonds (which is the main argument in the electron-counting model). The surface Ga atom, which has lost an electron, favors an sp^2-like hybridization, relaxes toward the bulk, and forms a more planar configuration with bond angles close to 120°. The dangling bond of arsenic is completely filled, and the As atom "prefers" to form bonds with its three p orbitals. Therefore the bond angle of the surface As atom is close to 90°, and the As atom relaxes outwards. These configurations resemble the bond geometry of small molecules like GaH_3 and AsH_3, and can be used to understand III-V semiconductor surfaces in general.[25]

Local-field and excitonic effects are neglected in calculating the reported dielectric functions; when both are included they might decrease (increase) the imaginary part of the dielectric function for high (low) energies.[26] However, within the LDA formalism used here, the exchange-correlation kernel does not carry enough information to help account for excitonic effects.

Figure 1(e) compares the calculated surface dielectric function anisotropy $\delta\varepsilon(=\varepsilon_{xx}-\varepsilon_{yy})$ of the As-terminated $\beta 2$ surface with that extracted from the RDS experiments reported in Ref. 2. The agreement is quite good; in particular, the peak energies and heights agree quite well for the main broad peak near 2.6 eV, and less well for the smaller peak near 4.2 eV. (These energies correspond to features in the real part of $\delta\varepsilon$.) In contrast, agreement with $\delta\varepsilon_\beta$ [Fig. 1(f)] is significantly poorer, which suggests that the $\beta 2$ arrangement may be the correct one for the (2×4) reconstruction.

In an often-presented simplified picture, the optical anisotropy of the surface is attributed to a larger polarizability along the dimer bond than perpendicular to it, and consequently the peaks of RD spectra are attributed to electronic transitions involving dimer states.[9] The origin of the electronic transitions responsible for the observed structure was determined by decomposing the calculated dielectric function into four parts, depending on whether the wave function of the initial and final state (of the particular transition contributing to $\delta\varepsilon$) is confined near the surface (s) or is further from the surface—in the subsurface or bulklike (b) region. (This division of states is similar to that in Ref. 19. If the square modulus of the wave function integrated over a spatial region corresponding to the surface and underlying atomic layer exceeds the same integral over the remaining atomic layers, such a state is classified as a surface state;
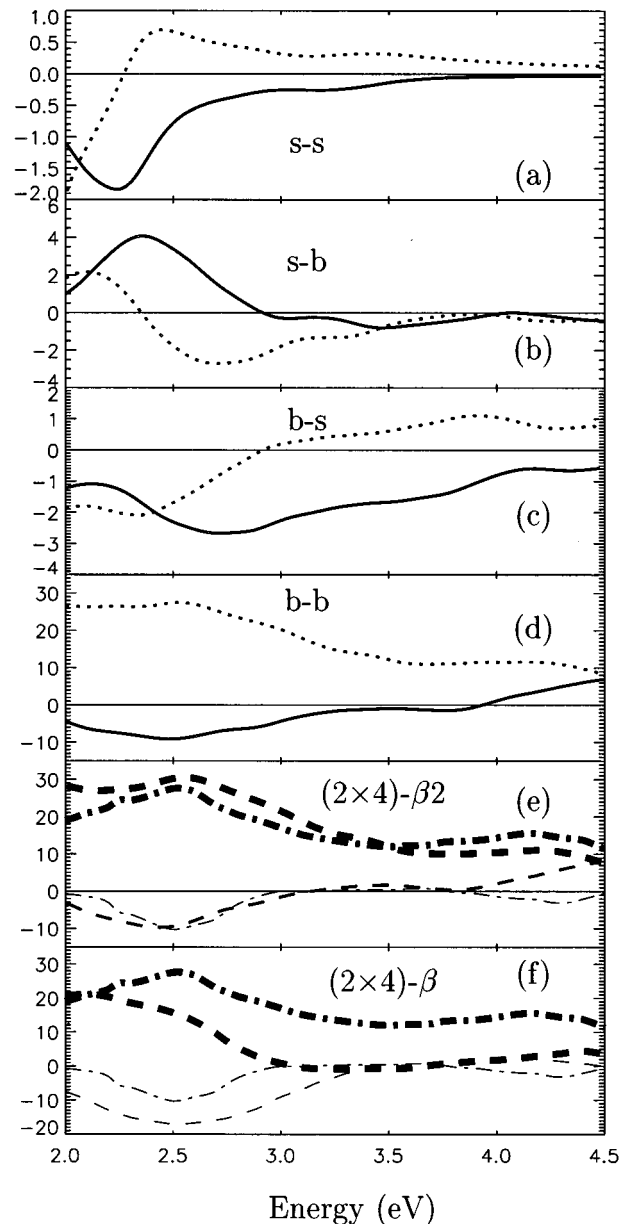

FIG. 1. The calculated anisotropy of the surface dielectric function for the (2×4) As-terminated GaAs (001) surface, decomposed according to the localization of initial and final states of the electronic transitions (s: surface and b: bulk), along with experimental data from Ref. 2. The dotted and solid lines in (a), (b), (c), and (d) are the real and imaginary parts of the calculated $\delta\varepsilon$ for the $\beta 2$ reconstruction, respectively. (e) and (f) compare the calculated total anisotropy and experimental results from Ref. 2 for the $\beta 2$ and β reconstructions, respectively. The dashed and dot-dashed lines in (e) and (f) are the calculated total anisotropy and experimental results from Ref. 2, respectively, and the thick and thin lines represent the real and imaginary parts, respectively.

otherwise it is called a bulk state. This criterion is used for both the β and $\beta 2$ reconstructions.) These components of $\delta\varepsilon$ are the surface-surface (s-s), surface-bulk (s-b), bulk-surface (b-s), and bulk-bulk (b-b) curves in Figs. 1(a)– 1(d). In each case, the states identified as surface states are localized on the atoms that are located on or near the surface

and they decay into the bulk exponentially. Tests with larger supercells with 14 atomic layers [instead of eight layers, for (2×4)-β] showed no appreciable difference in any of the calculated quantities, including the wave functions of the surface states.

The surface-surface transition anisotropy in [Fig. 1(a)] has structure near 2.4 eV, which is mostly canceled in the total calculated anisotropy [Fig. 1(e)]. The main structure in both the surface-to-bulk [Fig. 1(b)] and bulk-to-surface [Fig. 1(c)] anisotropies is near 2.6 eV, but they have opposite signs and cancel when summed. Most of the anisotropy in this energy range is found to be induced by bulklike states that are perturbed by the surface [Fig. 1(d)]. States localized at the surface dimers seem to give a minor contribution. The general similarity between $\delta\varepsilon_\beta$ and $\delta\varepsilon_{\beta 2}$ seems to support this idea even further. The feature around 4.2 eV is harder to analyze. The surface-surface terms do not have any component around this energy range, while the s-b and b-s terms are too small.

We have also examined how sensitive the dielectric function anisotropies are to the reconstructed atomic positions. The difference between $\delta\varepsilon$ for the electronic states of a non-relaxed (2×4)-$\beta 2$ surface (where the average force on the surface layer atoms >50 meV/Å, which is an order of magnitude larger than the convergence criterion) and a converged (2×4)-$\beta 2$ surface is found to be greater than that between relaxed β and $\beta 2$ reconstructions, which demonstrates that accurate reconstructions are necessary.

Figures 2(a)–2(d) shows similarly decomposed (s-s, s-b, b-s, and b-b) dielectric function anisotropies for the Ga-terminated (4×2)-$\beta 2$ reconstruction. The prominent feature for this surface is near 2.45 eV. The s-s term has some structure around 2.0–2.5 eV which does not show up in the total $\delta\varepsilon$. There is anisotropy near 2.2–2.4 eV in both the s-b and b-s contributions. In addition, the most prominent peak for the s-b component is near 3.6 eV, and for b-s it is near 2.4 eV. The total anisotropy [Fig. 2(e)] has a very strong bulk component, similar to the As-terminated surface. The calculated anisotropy is in good agreement with experiment for both the $\beta 2$ and β reconstructions [Figs. 2(e) and 2(f), respectively].

Since the dominant contribution in the dielectric function anisotropy for both the (2×4) and (4×2) reconstructions comes from the surface-perturbed bulk states, it is clear why the peaks in the RDS (and SPA) spectra of GaAs(001) are near the critical points for bulk GaAs. It is not unreasonable to expect that features associated with Ga-As (cation-anion) bonding, which occurs below the surface, would contribute to $\delta\varepsilon$ at energies near the dielectric function features of bulk GaAs, while features due to As-As (anion-anion) and Ga-Ga (cation-cation) bonding, on the surface, would not. This dominance of the surface-perturbed bulk states explains the observations of Uwai and Kobayashi[27] who studied the H_2 coverage dependence of the RDS signal during H_2 purging of As-rich GaAs(001) surfaces, and observed an RDS peak at this As-dimer signature energy well after all the As-dimers on the surface were broken. These authors have also recently shown that the appearance of the critical points of the bulk dielectric function in the surface reflectance spectra of GaAs
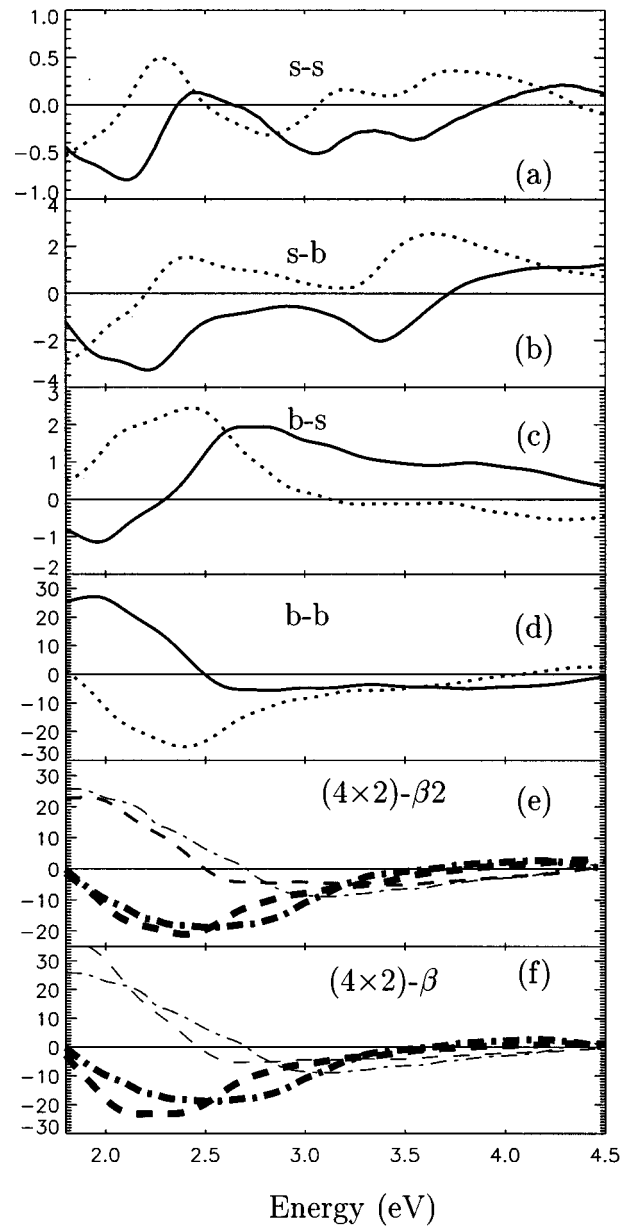

FIG. 2. Same as Fig. 1, for the Ga-terminated (4×2)-$\beta 2$ [(a)–(e)] and (4×2)-β [(f)] surfaces.

can be explained by assuming that light absorption is quenched at the surface because of the surface-terminated electronic wave functions.[28]

One possible reason why the reconstruction may perturb the bulk states in this manner is the large contraction of the top Ga-As layer for Ga-terminated surfaces and the expansion of this layer for As-terminated surfaces. Reference 19 reported the dominance of bulk states, i.e., the b-b contribution, in the calculated anisotropy of the GaAs(110) surface, for which there is large surface relaxation and no surface reconstruction (and therefore no surface dimers). Furthermore, one could expect that the states associated with the surface back bonds (which are expanded and contracted) compared to the bulk bond lengths would be the main source of the anisotropy (leading to features that are respectively

redshifted and blueshifted from the bulk energies). However, these bonds would be counted as ''surface'' states in the division in Figs. 1 and 2, and their contributions are too small and, in some cases, they have the wrong sign. Note that while RDS calculations in Ref. 13 showed that the $\beta2$ version of the (2×4) reconstruction seemed to be superior to the α and β versions, they also suggested that the surface anisotropy comes mostly from optical transitions between bulk valence-band states and unoccupied surface states, and not between bulk states only, which is what is found here. This difference with the current study may be due to the smaller number of special **k** points, smaller unit cell, and less stringent convergence criteria used in that study.

In conclusion, we have performed first-principles calculations of the atomic structure and anisotropy of the optical response of As- and Ga-terminated GaAs(001) surfaces. It is found that the anisotropy depends strongly on the details of the atomic structure, and a simple interpretation of the RDS data in terms of electronic transitions between well-defined surface states might be misleading. More specifically, spectral features of GaAs(001) observed using reflection-based surface spectroscopies correspond to transitions between bulk states that are perturbed by the surface rather than to transitions that are localized at the surface, at least for the β and $\beta2$ versions of the (2×4) and (4×2) reconstructions. This conclusion also seems to apply to other GaAs surfaces.

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