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Electronic structure of the GaAs(001)2×4 and GaAs(110) surfaces studied by high-resolution electron-energy-loss spectroscopy

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We compare, by high-resolution electron-energy-loss spectroscopy (HREELS), the electronic structure of the GaAs(110)1×1 surface and that of the GaAs(001)2×4 As-rich surface in the energy-loss region 0.5–5 eV. The HREEL spectra are interpreted in terms of realistic calculations. The spectral features above the gap are assigned to electronic transitions involving surface and/or bulk states. Losses at energies within the gap are associated to defect states at the surface. [S0163-1829(98)51236-2]

Unlike the stable, unreconstructed (110) surface of GaAs, the (001) termination of this crystal exhibits a variety of surface reconstructions,[1] roughly classified as As-rich and Ga-rich phases. They are sequentially obtained either by changing the stoichiometry of the outermost planes through specific heating procedures, or by epitaxial growth under suitable thermodynamic and kinetic conditions. Among others, the As-rich (001)-(2×4) and the Ga-rich (001)-(4×2) reconstructions are found to be the most stable ones. The 2×4 surface has been so far the most thoroughly investigated for its technological relevance in the epitaxial growth of GaAs-based devices. Most of the theoretical effort has been devoted to the determination of its complex atomic arrangement through experimental reflection high-energy electron diffraction (RHEED),[2,3] low-energy electron diffraction (LEED),[4–6] and scanning tunneling microscopy[7–10] (STM) data. The accepted model for the 2×4 reconstruction consists of a regular array of two dimers and two dimer vacancies[11] of As aligned along the $[\bar{1}10]$ direction. However, a full understanding of all the issues related to its surface electronic structure such as surface chemical reactions, Schottky barrier formation,[12,13] and morphology of the metal-semiconductor interfaces[14] has not been reached yet, either because the electronic and structural properties of GaAs(001) depend on surface preparation procedures and/or for insufficient surface sensitivity of many characterization spectroscopies. More recently, the problem of the identification of surface features has been addressed with surface-sensitive optical spectroscopies.[15–17] They offer the possibility, in contrast to electron spectroscopies, to monitor a surface during crystal growth without requiring ultrahigh vacuum. Recently, in numerous theoretical and experimental studies on the GaAs(001) surface, reflectance-anisotropy spectroscopy[15,18–20] (RAS) has been applied aiming at associating a specific anisotropic optical response to each surface reconstruction. Until now, however, the interpretation of the RAS spectra is still controversial, and the agreement among different experimental data is poor.

In this work we investigate by high-resolution electron-energy-loss spectroscopy (HREELS) the electronic structure of the (110) and (001) As-rich surfaces of GaAs in the energy loss region 0.5–5 eV, and assign on the basis of theoretical calculations the observed spectral features to excitations involving surface or bulk states, as well as defect states in the gap. The comparison among the spectra taken on the different crystal terminations demonstrates the capability of this technique to enlighten surface-related features.[21]

The HREEL spectra were measured at specular reflection with primary electrons of 20 eV incident at 45° from the sample normal. To improve the signal-to-noise ratio, the combined spectrometer and sample-limited resolution, measured by the full width at half maximum intensity of the quasielastic peak, was set at 44 meV. The highest loss signal for the (001) surface was obtained by aligning the parallel component of the electron momentum along the dimer bonds in the [110] direction. The (110) surfaces were obtained by cleaving *in situ* single-crystal ingots (n-type Si doped, $n = 4\times10^{16}\ \mathrm{cm}^{-3}$). Undoped GaAs (001) films, 0.5 μm thick were grown by molecular beam epitaxy (MBE) in As overflow on GaAs(001) substrates (n-type Si doped, $n=1\times10^{18}\ \mathrm{cm}^{-3}$) held at 600 °C. The ending surface of the film exhibited the RHEED pattern of the (001)2×4 As-rich phase. After the growth, the epitaxial films were capped at -10 °C with 0.5 μm of As for the transfer into the analysis chamber. The As cap was removed by annealing at 350 °C while monitoring the residual-gas partial pressure with a high-resolution mass spectrometer. A small amount of CO and CO_2, on top of the As cap, desorbed right before As. However, during the As decapping no increase in the CO and CO_2 partial pressures was monitored indicating that a cap layer is free from contamination. The As-rich surface reconstruction was obtained on the various samples by further annealing at 460–470 °C.

In Fig. 1 the STM image of a MBE sample annealed at 460 °C shows, on a large scale area (400×400 Å^2), bright streaks running along the $[\bar{1}10]$ direction of the 2×4 As-rich reconstruction. The line profile AA' on the magnified 60 $\times60$ Å^2 image reveals that the bright streaks, each containing two features (two dimers) with a spacing of 4.0 Å, are separated in the [110] direction by 16 Å, i.e., $4a_0$ being $a_0 = 4.0$ Å the lattice constant of the (001)1×1 surface. Along the $[\bar{1}10]$ direction (line profile BB'), the rows are made up of subunits separated by $2a_0$. Hence, the imaged unit cell—

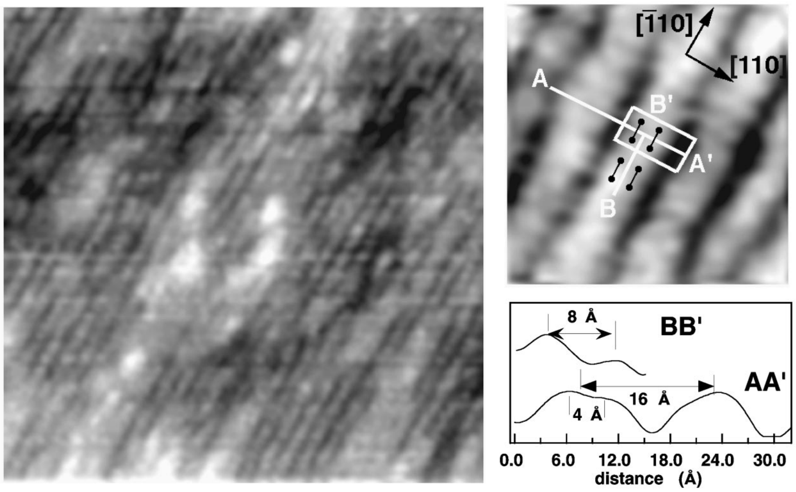

FIG. 1. STM filled states (bias$=-3$ V) images of a GaAs(001) 2×4 As-rich surface showing a 400×400 Å^2 and a 60×60 Å^2 area. The line profiles AA' and BB' depict the fourfold and twofold periodicity, respectively. The unit cell is also marked in the figure.

marked in the figure—has a 2×4 symmetry and is consistent with the ''two-dimer'' model[11] (α and $\beta2$ phases). The surface long-range ordering of all samples was checked by LEED.

The HREEL spectra of the (110) and (001) As-terminated surfaces, in the energy-loss range 0.5–5 eV, are plotted in Fig. 2(a) after normalization at 5 eV loss energy. In Fig. 2(b) the second derivative curves of the spectra locate the peak positions at the labeled energies, reproducible within ±0.1 eV, in all measured samples. The loss region corresponding to transitions at energies below the gap (1.42 eV) is enlarged in the inset in Fig. 2.

Surface and bulk excitations in the HREEL spectra have been identified on the basis of the theoretical loss function, shown in Fig. 3(a), calculated in terms of the dielectric function of the surface layer, according to the formulation[22] of Ref. 23. This quantity has been extracted from calculations of the dielectric function of a slab of N atomic layers ($N=20$ for the (001) surface, $N=31$ for the (110) surface) within the $sp3s^*$ semiempirical tight-binding method described in Ref. 24. The calculated reflectance anisotropy of the (110) and As-rich (001) surfaces for the accepted structural models of the two surfaces (the rotation-relaxation model for the former, the $\beta2(2\times4)$ model for the latter[25]) is in qualitative agreement with the experiments.[20,26] Assuming that the surface thickness corresponds to N_s atomic layers and subtracting the bulk dielectric function of the remaining layers from that of the slab, we determine the xx, yy, and zz components of the surface dielectric tensor. N_s is chosen in such a way as to assure the best convergence of the loss

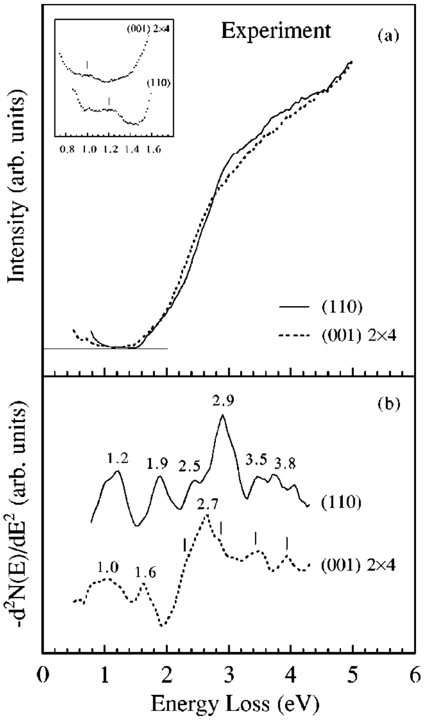

FIG. 2. (a) Experimental HREEL spectra of the (110), and of the (001)2×4 surfaces, in the energy loss range 0.5–5 eV. The spectra are normalized at 5 eV loss energy. (b) Second derivative curves of the spectra in the (a) panel. The marked peaks are discussed in the text. The energy-loss region below the gap is enlarged in the inset.

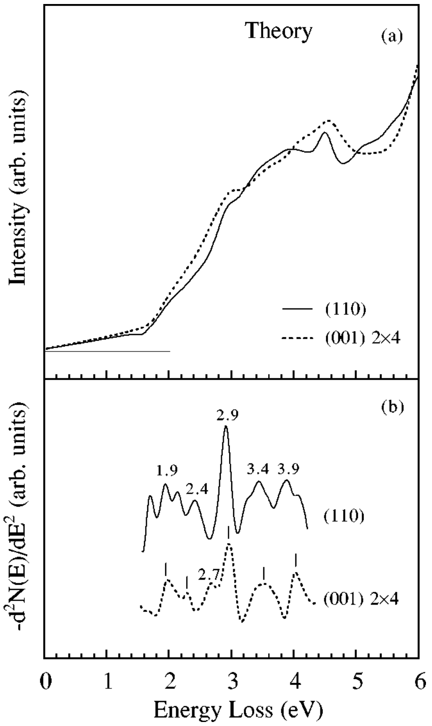

FIG. 3. (a) Calculated energy-loss spectra for the (110) and (001)2×4 GaAs surfaces. (b) Second derivative of the theoretical curves for comparison with the experimental spectra of Fig. 2.

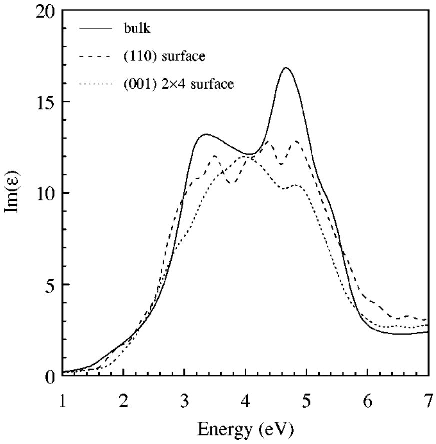

FIG. 4. Imaginary part of the calculated isotropic dielectric function of the surface layer for the (110) (long dashes) and (001)2×4 (short dashes) GaAs surface. Full line: imaginary part of the calculated bulk dielectric function.

spectra, that is, $N_s=4$ for the (110) surface, $N_s=6$ for the As-rich (001) surface. The imaginary parts of the dielectric functions of the surface layers of both surfaces are shown in Fig. 4. In order to take into account the deviation from the specular direction of the detected electrons (which affects the kinematical factor in a special way[23]) without carrying out the cumbersome integration of the resulting spectra over the solid angle of acceptance, we have calculated the spectra at an average off-specular deviation of 10°. The relatively large cone of acceptance of the electron analyzer washes out most of the surface anisotropy: for this reason, in Fig. 4 we have plotted the average dielectric functions of the two surfaces, which in practice determine the loss spectra, rather than the separate xx or yy components of the surface dielectric tensor.

The main structures of the measured loss function of the (110) surface, at energies above the gap, occur at 1.9 eV, 2.9 eV, and smaller peaks at 2.5 eV and above 3 eV (Fig. 2). This surface has been already investigated by many spectroscopies including HREEL,[27–29] differential reflectivity,[30] and inverse photoemission.[31] The peak at 2.9 eV, close in energy to the critical point E_1 of the bulk joint density of states, is attributed to bulk transitions in most studies,[27–29] even though a sizable contribution from surface excitations could be inferred by inverse-photoemission[31] and optical[30] data. This structure is clearly reproduced in the theoretical spectrum, shown in Fig. 3(a). It is also present in the calculated optical anisotropy and corresponds to the peak occurring at 2.7 eV in the room-temperature reflectance anisotropy spectrum.[26] Our tight-binding calculations, as well as recent *ab initio* calculations,[32] demonstrate a substantial (at least 50%) contribution to it of transitions across near-gap surface states, from As to Ga dangling bonds. A faint structure at 2.5 eV, barely visible in the integrated curves, is present in the second derivative of both the measured and calculated spectra. The 1.9 eV structure results from transitions across the bulk states at Γ, with the onset at the fundamental gap. The remaining features in the calculated loss are all due to transitions across surface-perturbed bulk states: the broad structure between 3 and 4 eV corresponds to the E_1 peak (occurring at 3.2 eV in the bulk spectrum of Fig. 4), the peak close to 4.5 eV to E_0', and the weak structures above 5 eV to E_2 (occurring at 4.8 eV in the calculated bulk spectrum). All these structures are seen in the experimental spectra of Fig. 2 at slightly higher energies than in the RAS spectrum,[26,32] as a consequence of the line-shape distortion that occurs in going from the dielectric to the loss function.

At the (001) surface, the loss region between 2 and 3 eV, more intense than in the (110) spectrum, gives rise to the prominent peak at 2.7 eV in the second derivative curve [Fig. 2(b)], also present in the calculated loss [Fig. 3(a)]. In the optical data,[15,19] two opposite interpretations have been provided for this peak. Eryigit and Herman[19] stated that the contributions to the optical anisotropy of transitions between surface states and between bulk and surface states are of opposite sign and tend to cancel out. Hence, the measured anisotropy at ∼2.7 eV is due to the surface-perturbed bulk-state excitations. In contrast, Kamiya *et al.*[15] assigned the broad structure at 2.5–2.8 eV in their reflectance-difference spectroscopy (RDS) data to transitions between filled As lone-pair states and unoccupied As-dimer antibonding orbitals.

Our calculation differs from that of Erygit and Herman for the treatment of the back surface, which is always different from the front one for the (001) orientation of III-V compounds: it is ideally terminated and hydrogen saturated in Ref. 19, but its contribution is embodied in the slab polarizability, which comes out to be not representative of the front surface alone. In our approach, instead, it is excluded from the calculation of the polarizability by means of a factor multiplying the matrix elements of the momentum operator, which is 1 at the front surface and 0 at the back surface. In spite of this difference, our calculations confirm the results of Erygit and Herman, i.e., the contribution of surface states to the spectral intensity between 2.5 and 3 eV is negligible. The transitions hypothesized by Kamiya and Aspnes occur at higher energies, close to 3.8 eV, with a very weak intensity. No evidence is found in the calculated spectra of a redshift of the onset from 1.9 to 1.6 eV, going from the (110) to the (001) As-rich surface. Hence also for this surface, we attribute the first above-gap structure to the transitions across bulk states near Γ. Probably the 0.3 eV shift with respect to the (110) surface is too fine a detail to be reproduced in our calculations, meant to bear only qualitative accuracy. Nevertheless, a remarkably good agreement is found between the calculated spectra shown in Fig. 3(a) and the experimental ones in Fig. 2(a). In both cases, the loss intensity of the (001) As-rich surface is predominant in the low-energy part of the spectrum, while that of the (110) surface is larger in the higher-energy part. The part of the spectrum corresponding to the E_1 and E_2 bulk structures is depressed as compared to the (110) surface. Correspondingly, the imaginary part of the surface-layer dielectric function (see Fig. 4) shows greatly reduced E_1 and E_2 peaks, mostly replaced by a peak (always due to surface-perturbed transitions across the bulk states) at 4 eV, from which the EEL peak at 4.5 eV originates. For both surfaces, surface-induced structures are present below 3 eV. In the case of the (110) surface, this structure embodies a substantial contribution of the transitions across surface states, while it is mostly due to transitions across surface-perturbed bulk states in the case of the (001) surface. However, also in this case the ultimate reason of the deviation of the surface dielectric function shown in Fig. 4 from the bulk one is the presence of the surface, meant as crystal termination with a well-defined atomic structure. These low-energy surface-induced transitions are slightly redshifted in the case of the (001) surface; this fact determines the larger intensity of the (001) loss spectrum below 3 eV appearing in Figs. 2(a) and 3(a).

As far as the energy-loss region below the gap is concerned, we found structures due to electronic transitions both on the GaAs(110) and on the GaAs(001) surfaces, as shown in the inset of Fig. 2(a). The fundamental gap of the GaAs(110) and (001) is free from surface states, therefore the peaks at 1.2 eV and 1.0 eV in the loss spectra can only be explained by the existence of defect states in the gap. The presence of defects on the clean GaAs surfaces has been revealed by many spectroscopies such as HREEL,[21] STM,[33] cathodoluminescence,[34] and nonlinear optical spectroscopy.[35] The defects at the surface and at the metal interfaces have a considerable basis in the Schottky barrier formation. By analyzing the HREEL spectral intensity of the gap structures in the metal-interface formation, it is possible to infer the growth morphology of the metallic film. This investigation was done for either the (110) or the $(001)2\times4$ As-rich and $(001)4\times2$ Ga-rich surfaces.[14,21]

In conclusion, we have comparatively analyzed the HREEL spectra of the (110) and (001) As-rich GaAs surfaces and assigned the loss structures to surface or bulk state excitations. The spectra are interpreted in terms of realistic calculations. Losses at energies below the gap are explained as due to the existence of defects at the surface.

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[1] The principal GaAs(001) phases identified by RHEED and/or STM, in order of decreasing As stoichiometry, are the 4×4; $\beta,\beta2,\alpha(2\times4)$; 2×4-$c(2\times8)$; 2×6; $\beta,\beta2(4\times2)$; 4×2-$c(8\times2)$; 4×6. More details can be found in the references cited in this work.

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