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Surface states at the GaAs(001)2×4 surface

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We have clearly evidenced the contribution of true surface states, in the range 1.8–2.5 eV, to the optical anisotropy of the GaAs(001)2×4 surface grown *in situ* by molecular beam epitaxy. These spectral features are well below the photon energy (2.9 eV) where bulklike anisotropies appear in coincidence with the E_1 bulk critical point. The surface character is established by studying the evolution of the reflectance anisotropy spectroscopy spectra versus oxygen exposure. The interpretation is strengthened by comparison with high-resolution electron-energy-loss spectra measured on the same surface and by first-principles density-functional theory calculations.

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After its early applications to study the bulk anisotropies of oxidized samples in air[1] and the optical properties of semiconductor surfaces in ultrahigh vacuum (UHV),[2] an important achievement of reflectivity anisotropy spectroscopy (RAS) was to monitor the growth of GaAs(001) samples during molecular beam epitaxy (MBE).[3,4] This significant development did not correspond to a real comprehension of the measured anisotropies, since a heuristic interpretation in terms of surface dimers was generally accepted. Although most part of detected features are measured above band gap and, in particular, in coincidence with bulk critical points, the measured spectra were originally explained as mainly originated from surface states just on the basis of an *a priori* statement: in cubic materials, the anisotropy measured between directions $[\bar{1}10]$ and $[110]$ of the (001) plane must be zero. Consequently, all the anisotropy terms ought to come from the surface. Furthermore, unrealistic calculations concurred to the supposed surface character of RAS signals.[5]

After about ten years of long-lasting discussions and experiments, nowadays the anisotropic features of clean GaAs(001)2×4 surfaces are interpreted in terms of bulklike states.[6–9] The surface acts as a perturbation of the otherwise isotropic bulk wave functions. Such a conclusion has been reached on the basis of new and realistic density-functional theory–local-density approximation (DFT-LDA) and quasiparticle calculations,[9] and by the observation that the main anisotropy structures of the As-rich phase always appear in coincidence with bulk critical points. Experimental findings also concurred to assign this bulk character: a directional strain externally applied to ZnSe(001) samples produces a RAS spectrum very similar to that of the clean surface, with peaks at the critical point energies.[10] Consequently, the intrinsic strain due to the directional surface bonds (dimer bonds) could induce measurable anisotropies, by breaking the symmetry of the underlying substrate.[11]

Other experimental studies have assessed the surface origin of RAS spectral features: the modification induced by gas (oxygen) in clean surfaces,[12] and, more recently, the study of the optical anisotropy of (001)-GaAs surface quantum wells.[11] A limit of the former experiment—inherent to the oxidation of the As-rich phase—is the continuous shift of the zero line observed during exposure to oxygen,[12] also detected in InAs(001)2×4,[13] which hinders the observation of minute modifications in the line shape. As a matter of fact, in Ref. 12 the authors conclude only on the dominant surface origin of the 2.9 eV peak and on the bulk origin of the 4.5 eV feature.

Recent experimental studies based on high-resolution-electron-energy-loss-spectroscopy[14,15] (HREELS) have well clarified the surface/bulk origin of the anisotropy. The high surface sensitivity of this spectroscopy[15] and the comparison with theory[16,17] have demonstrated that the HREELS peak at about 2.5 eV, appearing for loss along the $[110]$ direction and strongly sensitive to oxygen contamination, comes from surface states. Moreover, at energy higher than 2.7 eV the presence of bulk states is largely dominant. On the other hand, Paget *et al.*[18] have reported a DFT-LDA calculation of the RAS signal measured at GaAs(001)2×4 surfaces. The computed spectrum is represented summing four different possible contributions: surface-surface (SS), bulk-surface (BS), surface-bulk (SB), and bulk-bulk (BB), classified according to the location in real space of the initial and final states of the optical transition. A negative peak at about 2.5 eV, originating from transitions perpendicularly polarized to the As-As dimer axis, characterizes the SS term.

In a previous paper[19] on GaAs(001)$-c(4\times4)$, we demonstrated the power of combining RAS and HREELS spectroscopies on the same sample by exploiting their different surface-to-bulk sensitivities. The results have also clearly assessed the importance of characterizing surfaces freshly grown by MBE, which exhibit a higher quality with respect to those decapped or ion bombarded. For this reason we performed an experiment on the 2×4 reconstruction to check if a true surface contribution could be evidenced in RAS spectra. The results demonstrate that the only contributions from true surface states or surface resonances are located at energies below 2.6 eV, while for higher energies surface-modified bulk states dominate the spectrum.

The homoepitaxial growth of GaAs was performed on a Riber 32 MBE reactor on an *n*-type Si-doped ($n=1\times10^{18}$ cm^{-3}) substrate. After the removal, under As flux, of the native oxide layer at 630–650 °C, the substrate temperature T_s was kept at 560 °C during growth with a flux ratio $J_{\mathrm{As}}/J_{\mathrm{Ga}}\approx10$. After deposition of 0.4 μm of GaAs with a

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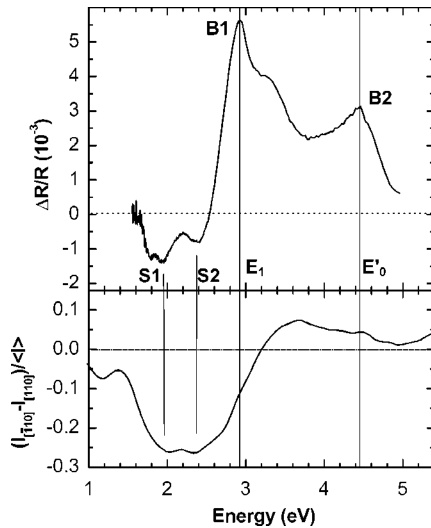

FIG. 1. (a) Reflectance anisotropy signal between the directions $[\bar{1}10]$ and $[110]$ for the clean GaAs(001)2×4 surface. (b) The relative intensity difference for the electron energy loss spectra along the $[\bar{1}10]$ and $[110]$ directions.

growth rate of 1.8 Å/s, the substrate was maintained, at the growth temperature, in As_4 flux into the reactor for 15 min while monitoring the surface reconstruction by reflected high-energy electron diffraction (RHEED). Then the sample was quickly quenched and transferred in UHV to the analysis chamber for the RAS and HREELS measurements. All measurements were performed at room temperature. Loss spectra were acquired using a fixed geometry with the electron beam of kinetic energy 15 eV impinging and being detected at $\theta=45°$ from the sample normal. RAS spectra were taken in the energy range 1.5–5.5 eV by using a single polarizer configuration. In such a way one measures $\Delta R/R=2(R_{[\bar{1}10]}-R_{[110]})/(R_{[\bar{1}10]}+R_{[110]})=2\,\mathrm{Re}(\Delta r/r)$, r being the Fresnel coefficient. Within the McIntyre-Aspnes model[20] for a surface layer of thickness $d\ll\lambda$ (λ being the wavelength of light), the RAS signal is given by

$$\mathrm{Re}\left(\frac{\Delta r}{r}\right)=\frac{2\omega d}{c}[A\Delta\varepsilon_s''-B\Delta\varepsilon_s'], \quad (1)$$

where $\Delta\varepsilon_s''=\varepsilon_s''^{[\bar{1}10]}-\varepsilon_s''^{[110]}$ and $\Delta\varepsilon_s'=\varepsilon_s'^{[\bar{1}10]}-\varepsilon_s'^{[110]}$ are the anisotropy of the imaginary and real parts of the surface dielectric function between the $[\bar{1}10]$ and $[110]$ directions of the surface, respectively. c is the speed of light, d is the thickness of the surface layer, and ω is the photon frequency. A and B depend upon the dispersive and dissipative part of the bulk dielectric function and are calculated from bulk optical functions. For a definition of A and B the reader is referred to Refs. 19 and 21.

We report in Fig. 1 RAS and HREEL spectra of the clean GaAs(001)2×4 surface. The following features can be identified in the RAS spectrum of Fig. 1(a): (i) a negative and broad double structure between 1.6 and 2.6 eV, (ii) a huge positive structure peaked at 2.9 eV (labeled $B1$) with a shoulder at 3.4 eV, (iii) a positive peak centered around 4.5 eV (labeled $B2$). By comparing our RAS spectra with those reported in the literature we note a general concordance in line shape, especially for $B1$ and $B2$: these two main structures are strictly related to the bulk critical points (surface-modified bulk states) E_1 and E_0', respectively. The positive shoulder at ~3.4 eV is similar to the feature found, at slightly higher energy, in the calculated spectrum of Ref. 9. However, no interpretation about it is provided by the authors. We point out that *the weak features occurring in the low-energy region (photon energy <2.6 eV) have never been evidenced before*. Previously published RAS spectra of (2×4) were measured on As-decapped samples[6,9,18,22,23] or, alternatively, during the MBE growth at ~500 °C:[4,24] in both cases such features did not occur. In As-decapped samples this may be justified by the lower reconstruction quality as already pointed out in recent works.[14,15] In MBE *in situ* measurements, the surface is well ordered, but the high temperature tends to broaden the structures and to reduce the anisotropy signal of the whole spectrum down to 0.2–0.3%. In the only MBE *in situ* measurements[25] where the low-energy features were observed, the spectrum was acquired at 80 °C: nevertheless, no discussion about them was provided by the authors.

The peaks $B1$ and $B2$ in Fig. 1(a), nearly coincident with the bulk critical points E_1 and E_0', respectively, are explained in terms of bulk transitions modified by the surface, although a little contribution from surface states was proposed by other authors.[11,18] As expected, they have no counterpart in the energy loss spectrum since the short probing depth of the electrons restricts the sensitivity of HREELS to the surface layer.[14,15]

On the basis of first-principles DFT-LDA calculations of the surface and bulk dielectric functions, the negative feature at 2.4 eV previously has been interpreted for both HREELS (Ref. 14) and RAS (Ref. 18) spectra as being due to transitions, polarized perpendicular to dimers ($q_\parallel$ along the $[110]$ direction), between states at the top As-dimer backbonds and unoccupied dangling-bond states of the second-layer Ga atoms. We now examine more closely the low-energy part of the RAS spectrum by means of calculations, carried out within DFT-LDA, using norm-conserving pseudopotentials and plane waves expanded to an 18 Ry cutoff. For the optical properties, we employ an accurate **k**-point sampling equivalent to 576 points in the 1×1 surface Brillouin zone (SBZ). In Fig. 2 we show the computed RAS for a ten-layer-thick slab of GaAs(001), taking variable integration depths over the slab dielectric functions.[26] The theoretical spectrum for six layers is in very good agreement with the experimental curve, at least in the line shape, as it clearly reproduces all the observed features (i)–(iii) of Fig. 1. The remaining discrepancies in the energy positions of the peaks mostly derives from the DFT-LDA underestimation of the band gap and from the neglect of many-body (excitonic and local field) effects in the calculation, which are the most severe approximations used (in comparison with the 18 Ry cutoff or our use of LDA rather than generalized gradient approximation, for instance).[27] The layer-resolved RAS technique[26] allows us to isolate the low-energy features: while the contribution from the top two layers gives rise to the $S2$ peak, which we identify with the 2.4 eV peak in the experiment, the $S1$ feature,

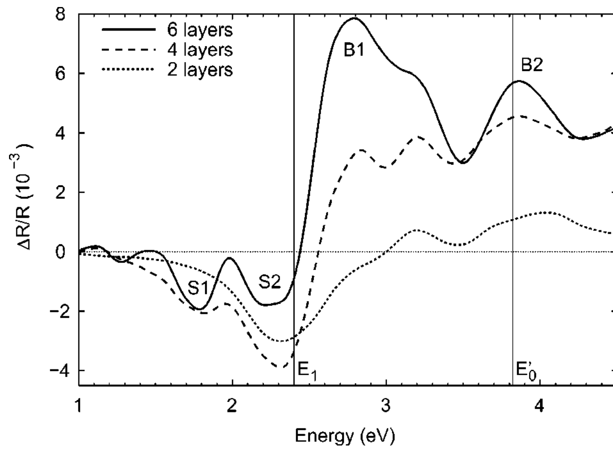

FIG. 2. Calculated RAS spectrum for the GaAs(001)-β_2(2 ×4) ten-layer slab within DFT-LDA, for different limits of integration over the surface dielectric function. A Lorentzian broadening of 0.15 eV has been used, which, along with the cutoff depth, influences the signal amplitude. Theoretical values for E_1 and E'_0 critical points are marked. No self-energy-type corrections to the DFT-LDA energies have been included in the spectra.

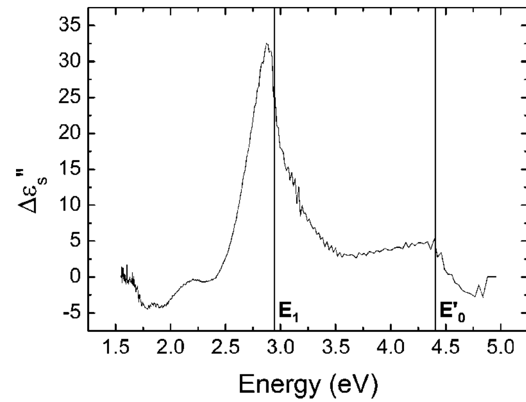

FIG. 3. $\Delta\varepsilon''_s$ vs photon energy for the clean GaAs(001)2×4 surface. $\Delta\varepsilon''_s$ is the anisotropy of the imaginary part of the surface dielectric function between directions [$\bar{1}$10] and [110], computed from the experimental curve of Fig. 1(a).

corresponding to the experimental structure around 1.9 eV, only clearly emerges when at least four layers are considered for d. The dominant transitions giving rise to the latter feature occur along Γ-J' in the SBZ: initial states are bulk states, lying close to the band edge, which have been perturbed by the surface layer—they have a sizable component on the third-layer As dimer—while final states are surface states of the second-layer Ga dangling bonds (as for $S2$), and antibonding orbitals of the third-layer dimer. Since the true surface states lie near the K point and outside the fundamental gap, it is likely that structures appearing in the RAS at very low energies should have components from surface-perturbed bulk states or surface resonances closer to Γ.

The relative difference, $\Delta I/\langle I\rangle$, of the HREEL spectra along the [$\bar{1}$10] and [110] directions, taken on the same surface, is presented in Fig. 1(b) and shows a broad double negative feature between 1.4 and 3.0 eV, which is in close correspondence to RAS features at energies lower than 2.6 eV. Given the high surface sensitivity of HREELS, we can directly assign—even without knowing the exact microscopic origin—the corresponding RAS peaks to transitions highly localized at the surface.

Equation (1) relates Re($\Delta r/r$) to the unknown anisotropy of the surface dielectric function. By means of the Kramers-Kronig (KK) analysis[21] one can obtain, from RAS data, $\Delta\varepsilon''_s$ and $\Delta\varepsilon'_s$ as well. In Fig. 3 we show the $\Delta\varepsilon''_s$ spectrum obtained in this way. There is a general agreement with the RAS spectrum, except for the disappearance of the shoulder at 3.4 eV. In fact, this feature is fictitious and originates from coefficients A and B.[19,21] When the absorption of the bulk is not negligible (in our case $B\neq 0$ for energies higher than ~3 eV) a contribution to Re($\Delta r/r$) is expected from the real part of the surface dielectric function [see Eq. (1)]. This contribution could give rise to structures in the RAS spectrum, which do not correspond to surface absorption, as was demonstrated for the InAs(001)2×4 surface.[21]

Further support to our interpretation of the RAS spectrum comes from the behavior of the spectral features after exposing the surface to molecular oxygen. In Fig. 4 we illustrate the RAS spectra decay as a function of oxygen exposure up to 10 KL (1 L corresponds to 1 s exposure to gas at a pressure of 10^{-6} Torr). Although progressive decay of the main structures at 2.9 and 4.5 eV occurs, nevertheless residual traces of these peaks are still visible after 10 KL, proving their bulk origin. The state-state decomposition of the $B1$ and $B2$ structures as reported in Ref. 18 allows us to estimate, respectively, ~25% and 47% of their intensity to deep transitions. These values are comparable with the percentages 27% and 35% achieved experimentally by means of the ratio between the peak intensities in the last oxidation and in the clean surface spectra. The bulk character of the structure at 2.9 and 4.5 eV is confirmed by the low decay constant η

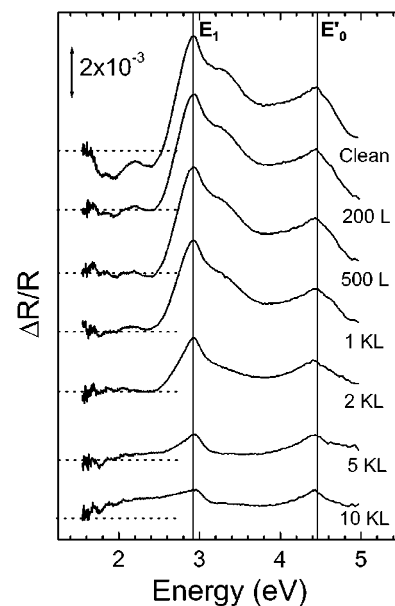

FIG. 4. RAS signal vs photon energy for the GaAs(001)2×4 surface exposed to increasing amounts of molecular oxygen.

(Ref. 28) that is about half of that observed for the 2.6 eV peak in the HREEL spectrum.[14] At variance with the critical points, the weak feature below 2.6 eV (Fig. 4) exhibits a high sensitivity to oxygen exposure. A strong reduction in intensity occurs already after an oxygen exposure of 200 L, showing a reactivity comparable to that observed in HREELS measurements.[14,29] This dramatic quenching across the full 1.8–2.6-eV range corroborates with the findings of the calculations, i.e., that the $S2$ and $S1$ features are strongly associated with the first- and third-layer dimers, respectively. STM and DFT-LDA studies[30] suggest that in the early stages of oxygen adsorption both surface dimers may be destroyed: following As-Ga backbond breaking, both topmost dimers are substituted by oxygen, while third-layer dimers are subsequently broken by the displaced As atoms. Unoccupied surface states at the second layer remain relatively undisturbed. Such a mechanism would account for the high surface sensitivity of the RAS features to oxygen absorption below 2.6 eV.

In conclusion, by means of comparative HREELS-RAS measurements and DFT-LDA calculations, we provide a complete interpretation of the RAS spectrum of GaAs(001)2×4. In particular we point out that the true surface transitions occur for energies below 2.6 eV and are mainly related to first-layer dimers ($S2$) and third-layer states ($S1$). Moreover, the higher sensitivity of such structures to oxidation in comparison to $B1$ and $B2$ provides a further proof of their surface nature.

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[27] The different surface and bulk contributions to B1 and B2 (discussed in the following) suggests that they may be influenced in different ways by, for instance, excitonic effects, or by size quantization (the latter causes the E_1 and E_0' transition energies to shift by +0.3 and +0.1 eV, respectively, for a ten-layer slab). We note, however, that for the GaAs(001)-$\beta2(2\times4)$ surface, the inclusion of quasiparticle corrections results in only minor modifications to the overall lineshape (Ref. 9).
[28] The intensity of peaks B1 and B2 follows, as a function of oxygen exposure x, an exponential law $I=I_0e^{-\eta x}$. The measured decay constants η for B1 and B2 are, respectively, 0.31 KL^{-1} and 0.24 KL^{-1}.
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