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Surface versus bulk contributions from reflectance anisotropy and electron energy loss spectra of the GaAs(001)-$c(4\times4)$ surface

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We report on the results of a combined experimental study of the optical anisotropy of GaAs(001)-$c(4\times4)$ surfaces grown by molecular beam epitaxy and examined *in situ* by reflectance anisotropy spectroscopy (RAS) and high resolution electron energy loss spectroscopy (HREELS). A correspondence is found between the spectral features detected with RAS and HREELS. The results clearly show that electronic states localized at the surface strongly contribute to RAS and HREELS signals below the E_1 bulk critical point (~3 eV), while above E_1 the contribution of bulk states (modified by the surface) becomes largely predominant in RAS. Progressive oxidation of the clean surface by molecular oxygen modifies the RAS features providing additional experimental evidence of their origin.

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It is well known that the earliest naive explanation of reflectance anisotropy spectroscopy (RAS) spectra of III-V semiconductors in terms of surface dimers transitions has already been abandoned and replaced by more realistic explanations.[1–6] Nevertheless, RAS spectra in these compounds are not yet fully understood, in particular it is not clear to what extent surface states contribute to optical anisotropy above the band-gap edge. Such doubts do not arise for cation-rich surfaces, in which the main features occur where the bulk is weakly absorbing. On the contrary, anion-rich surfaces exhibit structures close in energy to bulk critical points.[6,7] This fact has triggered a reinterpretation of the spectra based on realistic calculations and new experimental data that pointed out the prevailing bulklike nature for those structures.[2] However, the contribution from surface localized states has been recently reconsidered for GaAs(001)-$c(4\times4)$ and (2×4) reconstructions, thanks to high resolution electron energy loss (HREELS) measurements[8,9] and improved density functional theory (DFT) local density approximation (LDA) calculations.[2,4] In both cases the authors conclude that surface states should contribute to the anisotropy well below the E_1 bulk critical point.

A crucial breakthrough for solving this problem comes from the combined use of RAS and HREELS spectroscopies that have different sensitivity to bulk and surface. Low energy electrons have a much higher sensitivity to surface than photons, while, in optical measurements, the surface contribution is singled out from direct detection of absorption in the bulk gap[10–12] and/or by measuring the anisotropy signal between two directions that are isotropic in the bulk.[13] For example, in GaAs(001) crystals, anisotropy along orthogonal directions $[\bar{1}10]$ and $[110]$ is not expected: in such case any signal detected should be attributed to a surface effect. However, this does not imply that pure surface transitions take place, since bulk states give measurable anisotropies too, via the linear electro-optical effect at bulk critical points[14] or the existence of surface modified bulk transitions.[5,15]

To clarify the origin of the measured features of the GaAs(001) surfaces, we have applied RAS and HREELS to samples grown by molecular beam epitaxy (MBE). All measurements were performed in the analysis chamber connected in ultra high vacuum (UHV) to the MBE growth chamber. Previous comparative studies performed on decapped and as-grown MBE surfaces,[8,9] evidenced a greater surface quality for the latter; the As capping and decapping procedure, commonly applied,[16] degrades the electronic properties and the long-range order of the surface. Disorder originates from residual roughening upon arsenic desorption and the presence of mixed domains, as observed by scanning tunneling microscopy (STM).[17,18] These results prove the importance of studying GaAs and possibly other III-V epitaxial surfaces *in situ* instead of decapped surfaces to characterize their optical and electronic properties.

We have focused on the $c(4\times4)$ reconstruction of GaAs(001) that is the most rich in As among the stable reconstructions[19] and the most difficult to obtain starting from an As-capped sample. The accepted structural model for this reconstruction[20] is the "three As-dimers" model by Sauvage-Simkin *et al.*:[21] three As dimers, oriented along the [110] direction, sit on top of a complete As layer, resulting in an additional As coverage of 0.75 ML.

The results reported in this work allow us to discriminate between surface and bulk contributions in the optical spectra of the $c(4\times4)$ reconstruction and to single out the electronic transitions related to dimers. Surface anisotropies dominate the low energy part of the spectrum, while surface-modified bulk states prevail at higher energies (above 2.8 eV).

GaAs homoepitaxial films were grown in a Riber 32 MBE reactor over *n*-type Si-doped ($n=1\times10^{18}$), 500 μm thick GaAs(001) substrates mounted with In on a molybdenum holder locked to a modified 3-in molyblock. After deposition of a 0.6 μm thick GaAs epilayer the substrate was cooled down in As_4 flux within the MBE chamber while monitoring the surface reconstruction by reflection high-energy electron diffraction (RHEED). At about 500 °C the reconstruction converts from (2×4) to $c(4\times4)$, the latter being preserved down to room temperature. The sample was then transferred in UHV to the analysis chamber for the HREELS and RAS measurements.

Loss spectra were measured using a fixed geometry with the electron beam of kinetic energy 15 eV impinging and being detected at $\theta = 45°$ from the sample normal. All spectra were recorded with the sample at room temperature. The difference of the scattered intensity along the $[\bar{1}10]$ and $[110]$ directions, ΔI, at near-specular scattering, is proportional to the difference of the scattering cross section per unit solid angle Ω and unit energy loss $(\hbar\omega)$, given by[22]

$$\left(\frac{d^2S}{d(\hbar\omega)d\Omega}\right)_{[\bar{1}10]}-\left(\frac{d^2S}{d(\hbar\omega)d\Omega}\right)_{[110]} = A(\mathbf{k}_i,\mathbf{k}_s)\,\mathrm{Im}\left\{\frac{\tilde{\varepsilon}_{[\bar{1}10]}-\tilde{\varepsilon}_{[110]}}{(1+\tilde{\varepsilon}_{[\bar{1}10]})(1+\tilde{\varepsilon}_{[110]})}\right\}, \qquad (1)$$

where $\tilde{\varepsilon}$ is the effective dielectric function of the medium, $A(\mathbf{k}_i,\mathbf{k}_s)$ is the kinematical factor,[22] $\mathbf{k}_i$ and $\mathbf{k}_s$ are the incoming and scattered wave vectors. The tensor $\tilde{\varepsilon}$ can be described by the three-layer dielectric model,[23] where the surface is represented by a layer of thickness d. For additional details the reader is referred to Refs. 8 and 9.

RAS spectra were taken in the energy range 1.5–5.5 eV by using a single polarizer configuration, different from the more common version in which two polarizers are used.[24] Although both settings are equivalent, in the configuration we have used, the signal is less sensitive to alignment errors of the optical components. With this configuration one measures the real part of the complex RAS intensity along two orthogonal directions. Within the McIntyre-Aspnes model[25] for a surface layer of thickness $d \ll \lambda$ (λ being the wavelength of light), the RAS signal is given by

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

$\Delta\varepsilon_s''=\varepsilon_s''^{[\bar{1}10]}-\varepsilon_s''^{[110]}$ and $\Delta\varepsilon_s'=\varepsilon_s'^{[\bar{1}10]}-\varepsilon_s'^{[110]}$ being the anisotropy of the imaginary and real part 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. The A and B coefficients vs photon energy are computed from the experimental bulk dielectric functions[26] and, for GaAs, are reported in Ref. 27. An extensive discussion of A and B coefficients and their role in Eq. (2) is given in Refs. 12 and 27. Here we just note that A and B depend upon the dispersive and dissipative part of the bulk dielectric function respectively. It is worth remembering that the link between $\tilde{\varepsilon}$ and $\varepsilon=(\varepsilon_x,\varepsilon_y,\varepsilon_z)=(\varepsilon_s,\varepsilon_z)$, taking the scattering plane aligned along a principal lattice direction ($[110]$ or $[\bar{1}10]$ for the (001) surface), is

$$\tilde{\varepsilon}(\omega,q_\parallel)=\hat{\varepsilon}\frac{\varepsilon_b\cos(\tilde{q}d_s)-\hat{\varepsilon}\sin(\tilde{q}d_s)}{\hat{\varepsilon}\cos(\tilde{q}d_s)+\varepsilon_b\sin(\tilde{q}d_s)}, \qquad (3)$$

where $\hat{\varepsilon}=\varepsilon_z(-\varepsilon_i/\varepsilon_z)^{1/2}$ and $\tilde{q}=q_\parallel(-\varepsilon_i/\varepsilon_z)^{1/2}$ $(i=x,y)$, $q_\parallel$ being the parallel component of the transfer momentum in the surface (xy) plane.

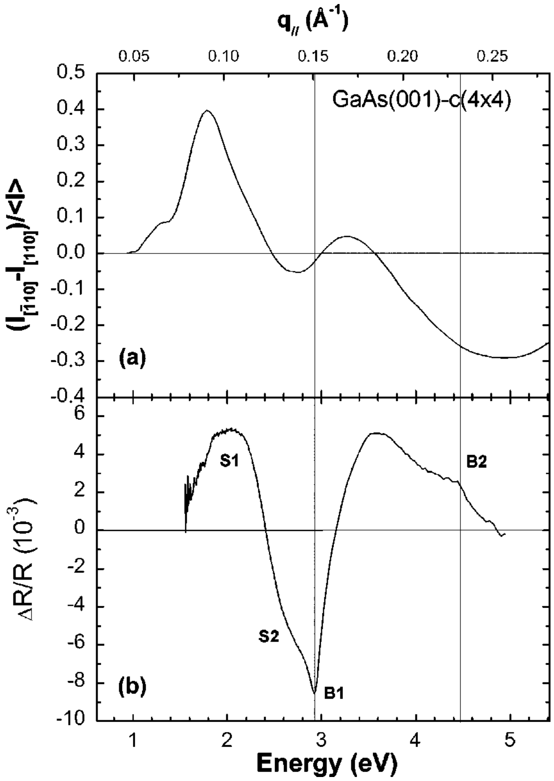

FIG. 1. (a) The relative intensity difference for the electron energy loss spectra along the $[\bar{1}10]$ and $[110]$ directions of the clean GaAs(001)-$c(4\times4)$ surface. The upper scale shows the magnitude of the transfer momentum $q_\parallel$ in the (001) plane. (b) Reflectance anisotropy signal between the directions $[\bar{1}10]$ and $[110]$ for the same surface.

We report in Fig. 1 HREELS and RAS spectra of the clean GaAs(001)-$c(4\times4)$ surface. The following features can be identified in RAS spectrum of Fig. 1(b). (i) A broad positive structured feature centered around 2.0 eV. It consists of two peaks at approximately 1.8 and 2.25 eV, as will be established from the comparison with the HREEL spectrum. (ii) A deep negative structure peaked at 2.9 eV with a shoulder at 2.7 eV. (iii) A broad positive peak centered around 3.6 eV. (iv) A stepped feature at 4.5 eV. As a result of the good surface quality, the total peak-to-peak intensity of the RAS signal is ~1.5% against typical values lower than ~1%.[1,2,4,7,13,18,28–31] Equation (2) relates $\mathrm{Re}(\Delta r/r)$ to the unknown anisotropy of the surface dielectric function. By means of the Kramers-Kronig (KK) analysis[6] one can obtain, from RAS data, $\Delta\varepsilon_s''$ and $\Delta\varepsilon_s'$ as well. However, since B is different from zero only above ~3 eV, the spectrum does not differ significantly from $\mathrm{Re}(\Delta r/r)$ up to this energy, as shown in Fig. 2.

In order to understand the origin of the observed RAS structures, is crucial the comparison with the HREELS spectra measured on the same surface. Such comparison is made by plotting in Fig. 1(a) the relative intensity loss difference spectrum $\Delta I/\langle I\rangle$. With the exception of the 1.2 eV peak, which is outside the experimental RAS energy range, one finds a correspondence between RAS and HREELS features up to 3.5–3.6 eV. On the basis of DFT-LDA first-principles

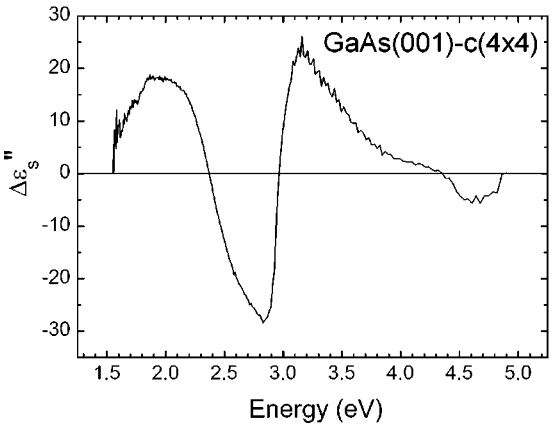

FIG. 2. $\Delta\varepsilon_s''$ vs photon energy for the clean GaAs(001)-$c(4\times4)$ surface. $\Delta\varepsilon_s''$ is the anisotropy of the imaginary part of the surface dielectric function between directions $[\bar{1}10]$ and [110], computed from the experimental curve of Fig. 1(b).

calculations of the surface and bulk excitations, the HREELS features have been interpreted[8] as follows. (i) The shoulder at 1.2 eV and the positive peak at 1.8 eV are due to transitions between surface bands. These low-energy transitions have been observed only perpendicular to the dimers and involve the As atoms of the topmost two layers. (ii) The positive shoulder at 2.25 eV and the negative peak at 2.7 eV arise from transitions localized on the topmost dimers and involve valence states resonant with the bulk states. By way of illustration, we show in Fig. 3 the calculated charge density plots resulting from the states mostly contributing to the transition at 1.8 eV.[8]

The broad positive peak in the RAS spectrum of Fig. 1(b) compares with the HREELS peak at 1.8 eV. This correspondence allows us to assign S1 to surface transitions polarized perpendicularly to the As-dimers in the topmost layer. We recall that this peak was previously recorded by RAS only on surfaces analyzed *in situ* in the MBE reactor.[7,13,29,32] On the contrary, it is *always* missing on As-capped samples, with the exception of Ref. 2 where a weak structure is detected at low temperature. Given the limits of the decapping procedure,[8,9] these findings are consistent with the surface nature of such structure or, at least, to its high sensitivity to the long-range order existing at the surface. In Ref. 2 the authors recognize the surface character of S1 without further commenting on its origin.

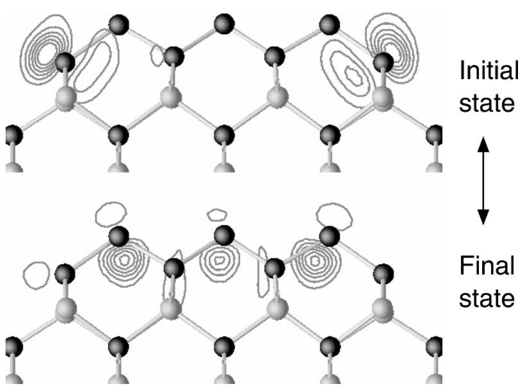

FIG. 3. Contour plots of squared wave functions for states involved in highest probability transitions at 1.8 eV. Plots are shown from the [110] direction for planes cutting through top layer (initial state) and second layer (final state) As atoms, respectively.

The peaks labeled B1, at 2.9 eV, and B2, at 4.5 eV, that are nearly coincident with the bulk critical points E_1 and E_0', respectively, are explained in terms of bulk transitions modified by the surface. As expected, they have no counterpart in the energy loss spectrum, because of the shallow probing depth of the electrons. In earlier RAS studies,[7,13] the presence of B1 has been correlated to As dimers. The shoulder $S2$ in Fig. 1(b) corresponds to the weak negative peak of the loss spectrum of Fig. 1(a). As discussed in Ref. 8, it is related to mixed transitions between bulk and surface states, the latter being localized on topmost dimers. This assignment agrees with recent calculations[2,4] and with the intensity behavior during oxygen exposure (see below).

The broad peak at 3.6 eV in Fig. 1(b), as expected by the theory,[2,4] is found in MBE samples inspected in situ after growth,[7,13,29,32] but not in As-decapped samples.[1,2,4,18,28,30,31] When the absorption of the bulk is not negligible (in our case $B\neq0$ for energies higher than ~3 eV) a contribution to $\mathrm{Re}(\Delta r/r)$ is expected from the real part of the surface dielectric function [see Eq. (2)]. This contribution could give rise to structures in the RAS spectrum, which do not correspond to surface absorption, as it has been demonstrated for the InAs(001)2×4 surface in Ref. 6. This could happen for the peak at 3.6 eV in the RAS spectrum as well. The calculated $\Delta\varepsilon_s''$ spectrum, as obtained from the KK analysis of the RAS spectrum, shows that the 3.6 eV peak has been removed leaving a peak at 3.2 eV (Fig. 2). In the HREELS spectrum there is a weak feature around 3.3 eV that may correspond to this one. Therefore, a genuine character for this peak is likely.

It is apparent from Fig. 1(a) that the loss intensity at 1.8 eV is larger than that of the peak at 2.7–2.9 eV, while the opposite is true in the optical spectrum in Fig. 1(b). This is consistent with both the lower sensitivity of HREELS to the bulk and with the strong bulk nature of the 2.9 eV peak.

RAS and HREEL spectra of Fig. 1 look markedly different at energies higher than 3.5 eV. Apart from a possible incomplete subtraction of the background in the energy loss spectrum, this occurrence might be in part related to the fact that $q_\parallel$ is not negligible (upper scale in Fig. 1). However, the disagreement is smaller if one compares the HREEL spectrum with the $\Delta\varepsilon_s''$ spectrum in which the bulk contribution is absent.

Further qualitative support to our interpretation of the RAS spectrum comes from the behavior of the spectral features after exposing the surface to molecular oxygen. Figure 4 shows that all features are gradually reduced for oxygen exposure up to 5×10^3L ($1L=10^{-6}$ Torr s), with the exception of the one at 4.5 eV (B2), which is ascribed to surface-modified bulk states transitions at the critical point E_0'.[1,2,4,5] At 10^4L the anisotropy signal almost vanishes (always with the exception of B2), with a residual peak at 2.9 eV (B1) superimposed to a positive background which shifts

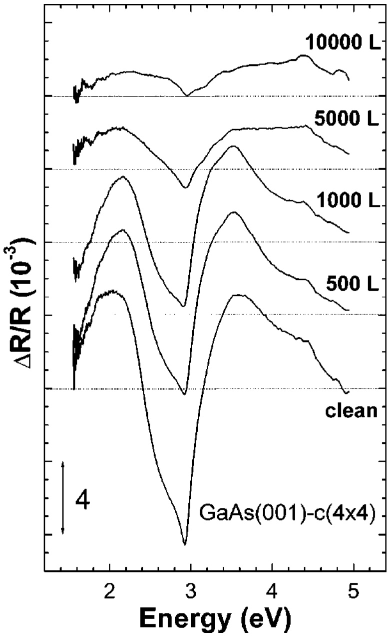

FIG. 4. RAS signal vs photon energy for the GaAs(001)-$c(4\times4)$ surface exposed to increasing amounts of molecular oxygen.

slightly the baseline upwards, a fact that has been also observed in the oxidation of the InAs(001)2×4 (Ref. 33) and GaAs(001)2×4 surfaces.[34] The behavior of B1 is consistent with the interpretation in terms of surface-modified bulk transitions at the critical point E_1. From a careful inspection of Fig. 4 we note that the low energy side ($S1$) of the 2-eV structure is more sensitive to oxidation than the high-energy side (at about 2.25 eV). This is consistent with the interpretation of the loss spectrum given in Ref. 8, where the weak 2.25-eV shoulder has been ascribed to mixed surface-bulk transitions. The oxygen sensitivity of the $S2$ peak is witnessed by the sharp change in the concavity of the spectrum around 2.7 eV, for oxygen exposures between 10^3L and 5×10^3L, in line with the above interpretation.

In conclusion, by comparing RAS and HREEL spectra measured in situ along the directions parallel and perpendicular to the dimers of high-quality GaAs(001)-$c(4\times4)$ surfaces, we have been able to distinguish the anisotropy signal due to surface localized transitions from those originating from bulk states modified by the reconstruction. The latter dominates the RAS spectrum close to the E_1 and E_0' critical point transitions at 2.9 and 4.5 eV, respectively, while they are absent in the loss spectrum which is only sensitive to the uppermost surface layers. In both spectra surface transitions are confined between 1.2 and 2.7 eV and involve the topmost dimers and the As atoms of the second layer. The intensity of these structures is reversed between HREELS and RAS, on account of the rather different probing depth of the two spectroscopies. Surface transitions in the bulk gap region, out of the RAS experimental energy range, have been recognized by HREELS at 1.2 eV. The sensitivity of all RAS structures to molecular oxygen up to exposures as large as 10^4L is fully consistent with expectations.

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