

Analysis of InAs(001) surfaces by reflectance anisotropy spectroscopy

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Reflectance anisotropy spectroscopy (RAS) was applied to study the reconstructed surfaces of InAs(001) at room temperature. Arsenic-capped InAs samples, grown by molecular beam epitaxy, were annealed in ultra-high vacuum. Low energy electron diffraction shows that, following As decapping, a 2×4 phase (As-rich) is obtained after annealing the sample at 340°C (10 mins), while a subsequent annealing at 450°C (15 mins) yields a 4×2 phase (In-rich). Using Kramers-Kronig relations, the anisotropy of the imaginary part of the surface dielectric function ($\Delta\epsilon_s''$) between $[\bar{1}10]$ and $[110]$ directions of the substrate has been obtained from RAS data. We present both the RAS and $\Delta\epsilon_s''$ spectra characteristic of (2×4) and (4×2) reconstructed InAs(001) surfaces, and interpret the appearing features in terms of surface-state transitions and bulk transitions (modified by the surface). The experimental data are compared with the case of GaAs(001). Below 3 eV, the presence of As and In dimers at the surface gives rise to optical anisotropies centered at 2.4 and 1.7 eV, respectively, with opposite polarizations depending on the dimer-bond direction. At higher energies, a structure related to E'_0 bulk critical point (at 4.4 eV) is visible.

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Optical spectroscopies, particularly reflectance anisotropy spectroscopy (RAS), have been intensively used to characterize GaAs(001) surfaces.¹⁻³ The experimental spectra exhibit structures, well defined in energy and sign, with a line shape characteristic of the particular stoichiometry and atomic structure at the surface. As a consequence, RAS has been definitely accepted as a useful spectroscopy to characterize the surface during growth or, more generally, after preparation, analogous to LEED (low-energy electron diffraction) and RHEED (reflection high-energy electron diffraction).^{1,2}

More recently, surfaces of other semiconductors have received increasing attention. In particular, InAs has been studied mainly as a consequence of the interest for quantum dots (QD) of this material on GaAs substrates.⁴ Also for InAs, the principally investigated surface has been the (001) surface,⁴⁻¹³ being technologically important for device fabrication.

The chemical and structural similarities between GaAs and InAs have been sometimes invoked to explain experimental results or to adapt to InAs structural models originally proposed for GaAs. For example, at present the (2×4) and (4×2) phases of InAs(001) are explained in terms of structural models very similar to the ones accepted for the corresponding GaAs surfaces.^{5,6,12} Nevertheless some peculiarities of InAs exist. For instance, phase transitions of different order for InAs or GaAs link the (2×4) surface to the (4×2) during molecular-beam-epitaxy (MBE) growth.⁷

Few papers have been published reporting results of optical spectroscopies applied on InAs(001) surfaces.⁸⁻¹⁰ "Chemical modulation optical spectroscopy" data have been reported in Ref. 10, while RAS has been applied to monitor the MBE growth process^{8,9} as well as the development of QD on GaAs(001) substrates.¹¹ Very recently, a new RAS study has been published about the oxidation at low temperature of clean InAs(001) surfaces.¹³ It is well known that tem-

perature has a strong effect on optical spectra, modifying line shapes and energy positions of the spectral features.¹⁴ Therefore, it is not straightforward to compare the results of Ref. 13 with those of the present work, taken at room temperature. However, an overall agreement exists.

We have studied clean InAs(001) surfaces obtained after decapping. Samples were MBE grown and then protected by a thick As layer to prevent contamination during transfer from the growth chamber to the ultrahigh-vacuum (UHV) analysis chamber. Capping/decapping is now a well-established technique to protect and successively prepare fresh surfaces in systems where an *in situ* growth facility is not available. This technique is commonly used for III-V compounds [GaAs,³ InP,¹⁵ GaP,¹⁶ GaSb (Ref. 17)].

Experimental data reported in this paper were obtained by using a RAS apparatus in the configuration with only one polarizer, different from the more common version of RAS in which two polarizers are used. We do not enter into the detailed differences between these two RAS apparatuses (see Ref. 18), and just note that with this configuration the signal is less affected by possible misorientation of optical components. On the other hand, with this configuration we can only measure the real part of the complex RAS signal. The RAS setup was placed in front of a strain-free quartz window. The results are given in terms of

$$\text{Re}\left(\frac{\Delta r}{r}\right) = 2 \text{Re}\left(\frac{r_{\bar{1}10} - r_{110}}{r_{\bar{1}10} + r_{110}}\right), \quad (1)$$

where r is the complex reflectivity coefficient.

Undoped InAs(001) films $0.7 \mu\text{m}$ thick were grown in the MBE laboratory of the University of Rome "Tor Vergata" using InAs substrates (n -type doped, $n < 2 \times 10^{16} \text{ cm}^{-3}$) provided by the Ioffe Institute of St. Petersburg. The substrates were held at 480°C in As_4 , overflow ($\text{As}_4:\text{In}$ atomic flux ratio 10:1). The final surface was annealed for 15 min in As_4 flux at growth temperature, and showed the RHEED pattern characteristic of the (2×4) As-rich phase. After growth, the

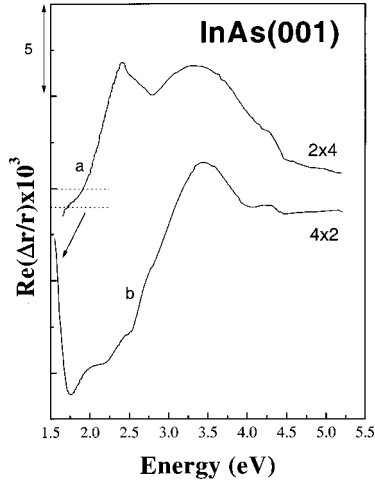


FIG. 1. Real part of $\Delta r/r$ vs photon energy for clean InAs(001) surfaces obtained after annealing at different temperatures: (a) $T = 340^\circ\text{C}$ (LEED pattern: 2×4); (b) $T = 450^\circ\text{C}$ (LEED pattern: 4×2). Each curve is referred to its own zero line.

epitaxial films were capped at -10°C with $0.5\ \mu\text{m}$ of Arsenic before transfer into the analysis chamber. On clean InAs(001) surfaces (2×4) [4×2] reconstructed, As-As (In-In) dimer bonds are aligned along $[\bar{1}10]$ ($[110]$).

The Arsenic cap was removed by annealing the sample at 320°C , while the pressure in the analysis chamber raised from 2×10^{-10} torr (base pressure) up to 5×10^{-8} torr. Subsequent annealing at 340°C for 10 min yielded a (2×4) LEED pattern. Further heating at 450°C for 15 min resulted in an excellent (4×2) pattern, with sharp LEED spots and low background intensity. All the temperatures were monitored with an infrared pyrometer. The overall error is estimated as $\pm 10^\circ\text{C}$. The RAS spectra were always recorded when the sample was at room temperature.

In Fig. 1 (curve *a*) we report the RAS spectrum of a clean InAs(001) surface exhibiting a clear (2×4) LEED pattern. The spectrum measured at the capped surface (not reported) is essentially structureless, as expected for an amorphous layer. After the cap has been desorbed, three main structural features become evident: a peak at 2.4 eV, a broad structure at about 3.5 eV, and a step at 4.4 eV.

The (2×4) is the most As-rich reconstruction we have obtained on the InAs(001) surface after decapping. We remind that the even more As-rich $c(4\times 4)$ reconstruction has been observed during MBE growth of InAs.¹⁹ However, by decapping, a $c(4\times 4)$ LEED pattern has never been obtained, similarly to the case of InP(001).²⁰ This is expected since the decapping temperature is higher than the substrate temperature needed in MBE to prepare the $c(4\times 4)$ phase (below 280°C , from Ref. 19).

Different phases (α , α_2 , and β_2) of the As-rich surface have been reported on the basis of theoretical expectations and experimental observations,^{5,12} all exhibiting a 2×4 periodicity. However, important differences exist between the corresponding structural models: in particular, the α and α_2 phases are believed to have two indium dimers per unit cell in the second layer, oriented along the $[110]$ direction. Consequently, we expect a negative anisotropy in the RAS spec-

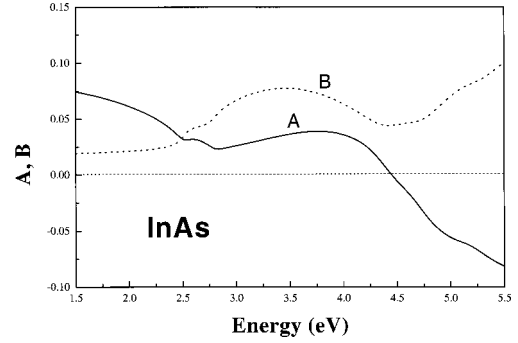


FIG. 2. *A* (full line) and *B* (dotted line) coefficients for bulk InAs vs photon energy. Optical data for InAs have been taken from Ref. 23. *A* and *B* have been defined in the text.

trum near 1.7 eV, the energy of the In-dimer line [see below, Fig. 1, curve *b*]. For the α phase of GaAs(001) this negative feature related to the Ga-dimer energy has been observed.²¹ Such a contribution is instead absent in our spectrum of the 2×4 surface [Fig. 1, curve *a*]. Moreover, we never observed a RAS spectrum for a 2×4 surface different from that reported in Fig. 1. Therefore, we conclude that in our case a β_2 reconstruction has been always obtained.

When the reconstruction pattern changes from (2×4) to (4×2), the RAS spectrum undergoes a strong variation [Fig. 1, curve *b*], developing a large negative curve with a deep peak at about 1.8 eV and a minor feature at 2.2 eV. A positive relic peak survives at 3.5 eV, while again a stepped structure is present at 4.4 eV.

For a surface layer of thickness $d \ll \lambda$ (λ being the wavelength of light), in the framework of the McIntyre-Aspnes model²² the RAS signal is expressed by

$$\frac{\Delta r}{r} = -\frac{4\pi id}{\lambda} \frac{\Delta \hat{\epsilon}_s}{1 - \hat{\epsilon}_b}, \quad (2)$$

where $\Delta \hat{\epsilon}_s$ is the anisotropy of the complex surface dielectric function and $\hat{\epsilon}_b$ is the bulk dielectric function.

This formula can be transformed—by splitting it into real and imaginary part—into the equivalent expression

$$\text{Re}\left(\frac{\Delta r}{r}\right) = \frac{2\omega d}{c} [A\Delta \epsilon_s'' - B\Delta \epsilon_s'] \quad (3)$$

$$\text{with } A = \frac{\epsilon_b' - 1}{(1 - \epsilon_b')^2 + \epsilon_b''^2}, \quad B = \frac{\epsilon_b''}{(1 - \epsilon_b')^2 + \epsilon_b''^2}. \quad (4)$$

$\Delta \epsilon_s'' = \epsilon_s''^{[\bar{1}10]} - \epsilon_s''^{[110]}$ and $\Delta \epsilon_s' = \epsilon_s'^{[\bar{1}10]} - \epsilon_s'^{[110]}$ are the anisotropies of the imaginary and real part, respectively, of the surface dielectric function between the $[\bar{1}10]$ and $[110]$ directions of the surface. ϵ_b' and ϵ_b'' are the real and imaginary part of the bulk dielectric function. c is the speed of light and ω is the photon frequency.

A and *B* are computed from experimental bulk dielectric functions,²³ and are shown for InAs in Fig. 2 vs photon energy. Here we just note that *A* (*B*) mainly depends upon the dispersive (dissipative) part of the bulk dielectric function.²⁴ For semiconductors, $B = 0$ holds below the energy gap.

Equation (3) relates the measured $\text{Re}(\Delta r/r)$ to the unknown anisotropy of the surface dielectric function. How-

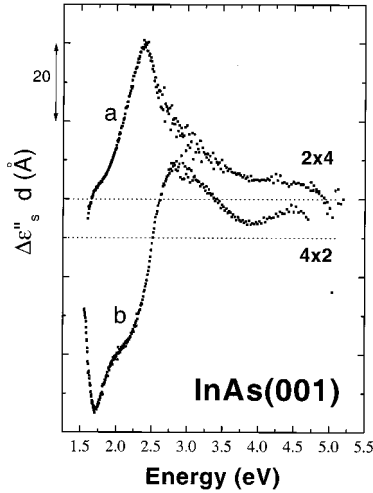


FIG. 3. $\Delta\epsilon''_s d$ vs photon energy for clean InAs(001) surfaces. $\Delta\epsilon''_s$ is the anisotropy of the imaginary part of the surface dielectric function between directions $[\bar{1}10]$ and $[110]$ computed from experimental curve reported in Fig. 1. d is the thickness of the surface layer. The corresponding surfaces have been labeled according to the respective LEED patterns: (a) 2×4 ; (b) 4×2 . Each curve has its own zero line.

ever, in order to obtain $\Delta\epsilon'_s$ and $\Delta\epsilon''_s$, we need an additional equation. In our case this second equation is given by the Kramers-Kronig (KK) relation.^{25,26} The latter is an integral equation that can be solved by turning it into a system of linear equations.²⁷

In Fig. 3 we report $\Delta\epsilon''_s d$ obtained from the $\text{Re}(\Delta r/r)$ spectra of (2×4) and (4×2) surfaces, shown in Fig. 1. Remarkable differences exist between the line shapes of $\text{Re}(\Delta r/r)$ and $\Delta\epsilon''_s d$. For a (2×4) surface, in $\Delta\epsilon''_s d$ only a peak at 2.4 eV is clearly evident (curve *a*, Fig. 3). For a 4×2 phase (curve *b*, Fig. 3), the dominant negative peak at low energy is present (the minimum is slightly shifted to 1.7 eV), plus a shoulder at 2.2 eV and a structure at 4.4 eV. In both cases, the feature at about 3.5 eV in $\text{Re}(\Delta r/r)$ has vanished in $\Delta\epsilon''_s d$.

From Eq. (3) it appears that only at photon energies where B is nearly zero (for InAs below about 1 eV), the real part of RAS signal is directly related to the anisotropy of the imaginary part of the surface dielectric function, giving a straightforward physical meaning to $\text{Re}(\Delta r/r)$. On the other hand, in III-V compounds $\text{Re}(\Delta r/r)$ is often measured in an energy range where the absorption of the bulk is not negligible ($B \neq 0$). This means that a deconvolution of both real and imaginary parts of the dielectric-function anisotropy is needed. Generally speaking, a contribution to the $\text{Re}(\Delta r/r)$ spectrum is expected from the bulk, via A and B coefficients: indeed in deriving $\Delta\epsilon''_s$ from $\text{Re}(\Delta r/r)$, we observe that some structures are removed, showing that they just originate from A and B . This is the case for the broad structure near 3.5 eV in Fig. 1.

$\Delta\epsilon''_s d$ is directly related to the optical transitions between electronic states at the surface. Therefore, in the following we will discuss only the $\Delta\epsilon''_s d$ spectra reported in Fig. 3.

For InAs, the E_1 and E'_0 bulk critical points are at 2.5 and

4.4 eV, respectively.²⁸ It occurs that the structures in the $\Delta\epsilon''_s d$ spectrum of (2×4) phase are near such critical points. However, we point out that the photon energy of the positive peak (2.4 eV) is close to but not coincident with the E_1 critical-point energy. Both its positive sign, meaning absorption along $[\bar{1}10]$ direction and its dependence upon annealing show that it is related to the As dimer termination of the surface.

However, the physical origin of this peak is unclear, as it is the nature of the corresponding peak for GaAs(001) near 3 eV in the (2×4) reconstruction. In both cases, there are some arguments in favor of a bulk-modified-by-the-surface origin and other arguments in favor of a true-surface-state origin. In both materials, the atomic structural model currently accepted for the (2×4) phase is the β_2 model with two top-layer arsenic dimers above an incomplete In layer, plus an As dimer in the third layer.⁵ Then two types of dimers are present in the unit cell. The result of a recent x-ray diffraction experiment²⁹ shows that in InAs(001) the dimers in the third layer are buckled and the ones in the first layer are not: therefore, they are not equivalent. We would expect that both dimers produce structures in RAS spectrum, possibly at different photon energies. However, in the spectrum of the clean (2×4) surface no other feature is visible in the neighborhood of the peak at 2.4 eV. We note that if the high-energy flank of the asymmetric 2.4-eV peak is interpreted as due to another unresolved feature, the latter would coincide with the bulk critical point $E_1 + \Delta_1$. The above discussion is seemingly against the true-surface-state interpretation. Moreover, in the case of GaAs(001) 2×4 theoretical studies of the optical anisotropies support the bulk origin of the main spectral features.^{30,31}

On the other hand, the strong sensitivity to oxygen contamination of the As-dimer peaks both in GaAs(001) (Ref. 32) and InAs(001) (Ref. 33) suggests that surface electronic states are involved in this transitions. A recent theoretical calculation of the surface electronic structure for the (2×4) phase of InAs(001) hints at surface optical transitions related to As-dimers at about 2.4 eV.¹²

For the (4×2) surface the $\Delta\epsilon''_s d$ spectrum is characterized by the deep negative minimum at 1.7 eV (Fig. 3, curve *b*), meaning a higher absorption for electric field parallel to $[110]$ direction, along which In-In bonds at the surface are aligned. Recalling Eq. (2) and the energy dependence of the B coefficient for InAs, we propose that in this case a true surface anisotropy related to electronic surface states contributes to $\text{Re}(\Delta r/r)$ below 2 eV.

In Fig. 3, curve *b*, a broad positive structure is peaked at 2.8 eV. However, considering that at 2.78 eV there is a bulk critical point, a surface modification of bulk states could be the origin of this anisotropy.

The positive feature at 4.4 eV in the case of the 4×2 reconstruction has an evident correspondence with E'_0 bulk critical point, similar to the case of the 4.5 eV structure for GaAs(001).³ Thus we propose that it is due to a modification of bulk wave functions induced by the surface.

As far as the structure at 4.4 eV is concerned, one could wonder that the similar feature in the (2×4) spectrum has reduced amplitude. This difference could arise from two

causes: (i) surface roughness, which changes from (2×4) to (4×2) (as tested by STM images^{7,34}); (ii) linear-electro-optical (LEO) contribution at E'_0 bulk critical point [our data for (2×4) do not display any LEO term at 2.5 and 2.78 eV].³⁵

The atomic structure of the (4×2) phase has not yet been established. Several models have been proposed. Among these, one is in agreement with STM images,³⁴ consisting of one In dimer per unit cell in the top layer plus two In dimers in the third layer.³⁶ Also in this case it is likely that distinct spectral features are produced by inequivalent dimers, thus we suggest that the minimum at 1.7 eV is due to In dimers of the third layer and the weaker minimum at 2.2 eV is due to In dimers of the top layer. Published data regarding deposition of Indium onto GaAs(001) surfaces substantiate this conclusion: when one In monolayer is annealed to grow an epitaxial layer, In dimers—aligned along the $[110]$ direction—yield a negative structure at 2.1 eV in RAS spectra.³⁷

Recently, a new model has been proposed for the cation-rich phase of GaAs(001), the ζ model,³⁸ qualitatively different from the so far discussed reconstructions. If we make the hypothesis that an analogous structure is valid for InAs,

again three In-dimers are present in the unit cell: one in the first layer, two in the second.

Finally, we want to address the issue of the comparison between the InAs and GaAs (001) surfaces, given the resemblance between the corresponding RAS spectra. In particular, the peaks at 2.4 eV (1.7 eV) for the $2 \times 4(4 \times 2)$ of InAs correspond to the 2.9 eV (2.2 eV) peak in the $2 \times 4(4 \times 2)$ of GaAs. Moreover, the peaks at about 4.5 eV in GaAs and InAs are clearly similar, as already pointed out. Therefore, one is led to speculate that the physical origin of all these peaks is the same in both materials. The situation can be summarized as follows. In the cation-rich phases the prominent (negative) RAS structures are well below the E_1 bulk critical point, therefore they clearly involve surface states related to dimers and/or dangling bonds. On the contrary, in the anion-rich phases the relevant anisotropies are very close to the E_1 critical point (in both materials). This finding points to a dominant bulklike character of these transitions, although a concomitant surface contribution cannot be excluded. Theoretical calculations of the optical properties for GaAs(001) and electronic properties for InAs(001) are not conclusive about this point.

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