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Surface and bulk origin of the optical anisotropy of As-rich GaAs(001) and $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}(001)$

D. Paget,[1] C. Hogan,[2] V. L. Berkovits,[3] and O. E. Tereshchenko[4]
[1]*Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau cedex, France*
[2]*Dipartimento di Fisica and INFM, Università di Roma "Tor Vergata," 00133 Roma, Italy*
[3]*A. F. Ioffe Physico-Technical Institute, 194021 Saint Petersburg, Russia*
[4]*Institute of Semiconductor Physics, Novosibirsk State University, 630090 Novosibirsk, Russia*

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We show experimentally and theoretically that the characteristic line at 3 eV in the reflectance anisotropy (RA) spectra of As-rich (001) GaAs has a mixed bulk and surface origin. The experimental observations rely on the analysis of the position of this line as a function of indium concentration in $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$. Up to $x \approx 0.5$, the peak energy dependence follows that of the nearby E_1 *bulk* optical transition, which shows that the line is not of pure *surface* character. The same conclusion is drawn from the mere fact that the line position depends on x since, because of indium surface segregation and bond length conservation, the energy of a purely surface-related transition should weakly depend on bulk composition. The combined relevance of surface states and surface-perturbed bulk states is shown by an *ab initio* density functional theory local dnesity approximation calculation of the RA spectrum of As-rich (001) GaAs, which also explains the observed oxygen-induced changes of the RA spectrum.

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I. INTRODUCTION

It is of interest, both for fundamental reasons as well as for applications to epitaxial growth and surface chemistry, to clarify the origins of reflectance anisotropy (RA) spectra of clean (001) surfaces of III-V semiconductors such as GaAs and InAs.[1–3] For anion-rich GaAs surfaces exhibiting the $(2\times4)/c(2\times8)$ reconstruction, there has been a long-lasting controversy as to the origin of the optical anisotropy: in addition to a signal near 4.5 eV, which corresponds to a bulk optical transition at the E_0' critical point, one observes a characteristic line near 3 eV—i.e., near the E_1 bulk transition—for which various interpretations have been given.[1,4] Theoretical studies[5] and *ab initio* calculations[6] conclude that the line is related to optical transitions in the bulk or near surface layers of the bulk; tight-binding calculations indicate that the initial state of the transition is localized at As surface dimers, while the final state is hybridized with bulk states.[7] From an experimental point of view, the RA signal at 3 eV is strongly sensitive to oxygen adsorption, which suggests a surface origin or a combination of both.[4] A recent study using surface quantum wells concludes that the corresponding signal is composed both of bulklike and of surfacelike transitions.[8]

In the present work, we resolve the above contradictions and clarify the nature of the states which participate in the optical transitions at 3 eV, using density functional theory local density approximation (DFT-LDA) *ab initio* calculations for GaAs and by experimentally monitoring the peak energy of $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$ alloys as a function of In concentration. The addition of a given amount of In gives qualitative insight into the origin of the optical transition, since the energy of a bulk-related optical transition is expected to depend on x in the same way as the nearby E_1 bulk critical point. These alloys also provide a test for the importance of surface optical transitions: because of indium segregation,[9,10] the composition of the surface layer weakly depends on indium concentration.[11] Surface-related features in the spectrum should therefore appear at an energy essentially independent of x.

II. EXPERIMENT

We have used epitaxial $\mathrm{Ga}_{0.47}\mathrm{In}_{0.53}\mathrm{As}$ layers, molecular beam epitaxy (MBE) grown on InP, and $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$ layers, metal-organic chemical-vapor deposition (MOCVD) grown on GaAs, with x equal to 0.13 and 0.26. For the latter layers, in order to avoid spurious strain-induced RA signals at the energy of bulk transitions,[12] we have chosen a thickness of 1 μm which is significantly larger than the known minimum thickness for strain-free surfaces,[13] estimated to be 70 nm and 20 nm for $x=0.13$ and $x=0.26$, respectively. For the InAs sample, we have chosen bulk material. In order to avoid electric-field-induced RA features at the energies of bulk optical transitions,[14] we have chosen undoped crystals, with a residual impurity concentration of the order of 10^{16} cm^{-3}. The RAS setup[15] and UHV system[16] are standard. Surface preparation has been performed using HCl-isopropanol treatments, known to give clean high quality GaAs (Ref. 17) and InAs (Ref. 18) surfaces. Under annealing of the as-treated surfaces, at a temperature of the order of 550 K, adsorbed elements were removed and the As-rich reconstruction appeared, as controlled using RA spectroscopy under anneal. A low-energy electron diffraction (LEED) investigation, performed in an independent setup, has allowed us to observe, at the same annealing temperature, the (2×3) reconstruction characteristic of indium surface segregation.

Shown in Fig. 1 are the RA spectra in the energy range of the main positive peak, taken at 125 K in order to reduce the linewidth. This peak is observed near 2.95 eV and 2.35 eV in the well-known spectra of GaAs (curve A) and InAs (curve E), respectively. Also observed are small signals, marked by arrows in curve A, at the energies of the E_1 and the $E_1+\Delta_1$ bulk optical transitions.[14] Intermediate curves B, C, and D show the $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$ RA spectra for x values of 0.13,

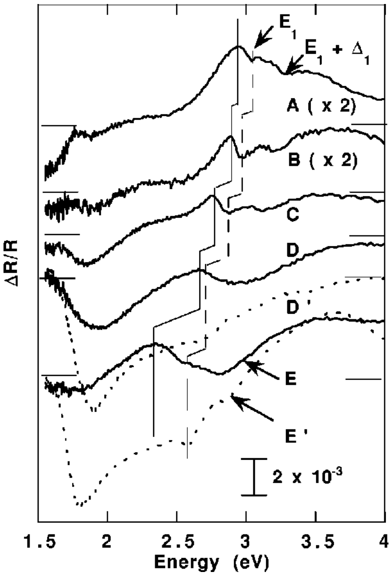

FIG. 1. RA spectra of As-rich surfaces, taken at 125 K. Curves A and E show the extreme cases of GaAs and InAs, while curves B, C, and D correspond to $Ga_{1-x}In_xAs$, with x equal to 0.13, 0.26, and 0.53, respectively. The solid line shows the evolution of the main positive peak. Curves D′ and E′, shown by dotted lines, are the RA spectra of the cation-rich surfaces and are used instead of curves D and E for determining the E_1 optical transition energy. The dashed line shows the evolution of the E_1 bulk optical transition.

0.26, and 0.53 respectively. The main line continuously shifts from its GaAs position to its InAs one. The negative signal observed near 2 eV in curves C and D may be caused by As dimers in the [110] direction, which are present on the In-segregated (2×3) surface reconstruction.[11] Also shown for each spectrum is the position of the structure due to the E_1 bulk optical transition, which appears as a slight dip on the high-energy edge of the signal. This feature has a well-known origin and can be attributed to a residual surface electric field[19] or to stress,[20] which are known to generate derivativelike signals.

It is clear that the peak position follows that of E_1, at least up to curve C. For larger indium concentrations, the E_1-related structure cannot be easily resolved. In this range, the E_1 value can be determined from the RA spectra of the cation-rich surface, obtained by annealing at higher temperatures of 750 K (curves D′ and E′). The results are summarized in Fig. 2. The E_1 dependence is qualitatively similar to what has been measured independently at room temperature.[21] Up to $x = 0.53$, the position of the RA peak is similar to that of E_1, which confirms that the electronic states involved in the optical transition have a significant bulklike character. Note that, for InAs, the picture seems to be different. We observe an increase in broadening, which is visible on the low energy side of the line. Furthermore, the difference between the peak position and the E_1 energy is as large as 0.2 eV, which suggests an increased role of surface states. This result is in agreement with the observation that the line is already formed, at an energy close to that observed for bulk InAs, for InAs layers of two monolayers (2 ML) thickness grown on GaAs.[22]

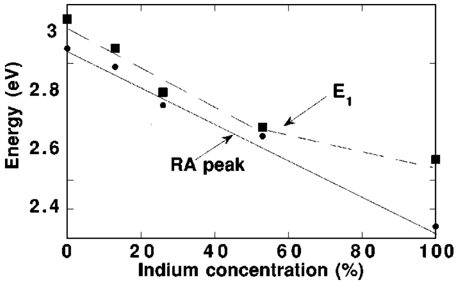

FIG. 2. Energy position of the main line as a function of x, together with that of the E_1 optical transition. Solid and dashed lines have been drawn to guide the eye.

In fact, because of indium surface segregation, the mere dependence of the peak position on concentration indicates that it is not purely of surface character. It has been found independently[10,11] that the surface is composed of building blocks for which the structure is independent of indium concentration, with a top layer composed of As and a second layer composed essentially of indium atoms. Thus, the only effect of indium concentration on the surface local geometry is through changes of lattice constant. The As dimer bond length—shown in tight-binding calculations of GaAs to be the key parameter for determining the energy of *surface* optical transitions[7]—should be independent of x, because the bond length is mainly determined by the chemical nature of the atoms participating in the bond and weakly depends on the lattice constant. This latter fact has been shown in the bulk.[23] For As-rich surfaces of InAs and GaAs,[24] the dimer lengths d are found to be equal within better than 1%, whereas the lattice parameters differ by 7%. In the case of an optical transition of pure *surface* origin, where the peak energy is assumed to scale like $1/d^2$,[7] we calculate from the experimental results that this length should increase by approximately 12% between GaAs and InAs, which is in contradiction with the latter findings.

III. INTERPRETATION

The RA sensitivity to oxygen adsorption[4] suggests that surface states also play a significant role, which seems to contradict the above results. In order to identify more precisely the relative contributions of surface and bulk states in the spectra, we have performed an *ab initio* DFT-LDA calculation of the optical anisotropy of clean (2×4)GaAs(001) with a β_2 unit cell. A slab of ten layers of GaAs and six layers of vacuum was used, with a plane-wave energy cutoff of 13 Ry. The surface structure was fully optimized using a single **k** point, while 32 **k** points were used in the calculation of the optical properties. The GaAs slab was terminated with fractionally charged hydrogens, and we employ a real-space cutoff function to remove the contribution of the back layers.[25] A scissors operator shift of 0.8 eV was used to enable meaningful comparison of energies with experiment.[6] Further details will be given elsewhere.[26]

Results of the calculation are shown in Fig. 3. The total calculated spectrum, shown in curve A, is similar to the RT experimental one, shown in curve J, except for a blueshift of about 0.5 eV in the 3–4 eV energy range.[27] Shown in the

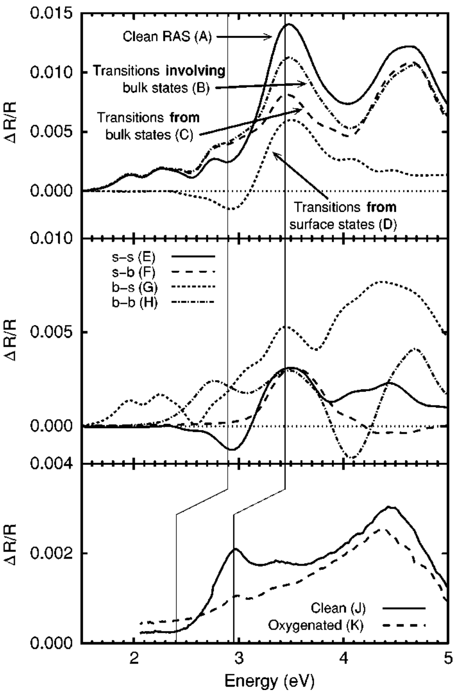

FIG. 3. Top panel: Calculated RA spectrum (A) of (2×4) GaAs(001), and total bulk-related part (B) of this signal, i.e., from bulk-bulk+bulk-surface+surface-bulk transitions. Also: decomposition of the total RA spectrum into the sum of bulk-bulk+bulk-surface (C) and surface-surface+surface-bulk (D) transitions. Middle panel: isolated contribution from surface-surface (E), surface-bulk (F), bulk-surface (G), and bulk-bulk transitions (H). Bottom panel, taken from Ref. 4: experimental spectrum of clean surface (J) and same after oxidation (K). The vertical lines indicate the correspondence between calculated and experimental peak energies.

middle panel of Fig. 3 is the decomposition of the signal between transitions involving bulk and surface states. We define the surface layer to be three to four atomic layers thick, thus encompassing the first- and third-layer dimers and their backbonds. The four corresponding curves exhibit peaks at 3.4 eV. This shows that the peak (experimental energy 2.95 eV) has a mixed surface and bulk origin. The pure surface (s-s) and pure bulk (b-b) contributions each comprise approximately 20% of the peak magnitude, while the rest is due to mixed (s-b and b-s) transitions.

The above decomposition allows us to interpret qualitatively the indium-induced shift of the peak, at least for concentrations smaller than 0.53. (The behavior at larger indium concentrations reveals a distinct mechanism which cannot be explained by the present considerations on GaAs. Its explanation requires a calculation of the InAs spectrum, which is outside the scope of the present work.) The bulk-related contribution, defined as that for which the energy position depends on the bulk band structure, is given by the sum s-b $+b$-$s+b$-b, and is shown in curve B of Fig. 3. The remaining signal (s-s, curve E) weakly depends on the bulk band structure. Since the latter signal represents less than 25% of the total signal, it seems natural that the peak position will tend to follow the bulk band structure.

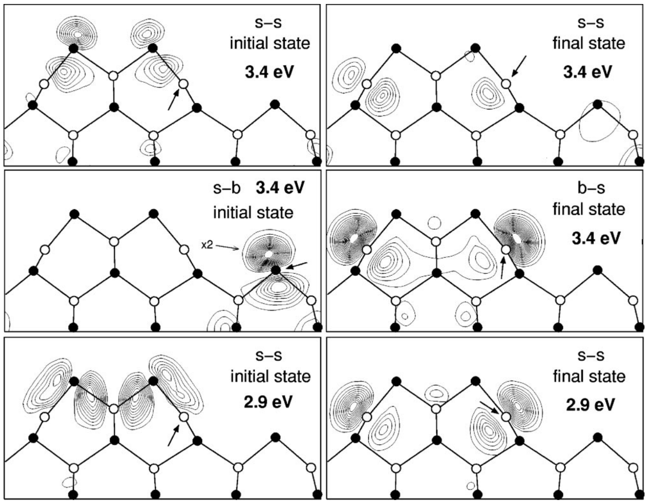

FIG. 4. Squared wave functions of surface states with largest contribution to optical transitions at 2.95 eV and 3.4 eV (theoretical energies). The contour spacing is 2.1×10^{-4} bohr^{-3} in each panel, except in the s-b plot, where it is 4.2×10^{-4} bohr^{-3}, as shown. Contour planes are perpendicular to $[110]$ and cut through the atoms indicated by arrows.

We now explain the RA sensitivity to oxygen adsorption, which we recall in curve K of Fig. 3, taken from Ref. 4. In this curve, the signal at the E_0' bulk optical transition is only slightly reduced. The peak at 2.9 eV decreases significantly, but is still visible. A slight oxygen-induced *increase* of the signal is also observed experimentally in the 2.0–2.5 eV range. The oxygen-induced effect can be understood by the following: excited, electronegative, oxygen atoms should mostly react with negatively charged surface sites corresponding to occupied electronic states, and therefore such adsorption should quench transitions corresponding to (occupied) surface-related initial states, as involved in the sum of the s-$s+s$-b contributions. Conversely, transitions involving (unoccupied) final surface states—such as in b-s transitions —should be relatively unaffected, in the same way as transitions involving only bulk states. More precisely, a recent analysis[28] suggests that oxygen displaces top-layer As atoms but leaves the dangling bonds of the second layer Ga atoms relatively unaffected, shown below to be final states of the optical transition.

The above facts suggest that interpretation of the oxygen-induced effects requires a different combination of the four elementary contributions from that used to interpret the indium-induced shift of peak energy. Shown in curves C and D are decompositions of the total calculated signal into the corresponding sum of b-$b+b$-s contributions and the sum of the residual s-$s+s$-b contributions, respectively. As expected, all the observed oxygen-induced effects (the decrease of the signal at 2.95 eV, its relatively small change above 4 eV, and even its increase below 2.7 eV) can be qualitatively explained by a quenching of the signal shown in curve D. The observed increase of the signal below 2.7 eV is due to oxygen-induced quenching of the s-s optical transitions, which, in agreement with the results of Schmidt *et al*,[29] contribute to a negative signal in curve E at the theoretical energy of 2.9 eV. Finally, as seen in curve K, the positive peak at 2.95 eV has not completely disappeared after oxidation. The residual signal is due to the part of the signal originating from bulk initial states (curve C), which are assumed to be unaffected by oxygen adsorption.

Finally, we describe in detail the surface states responsible for the anisotropy. Contour plots of the squared wave functions corresponding to dominant transitions at 3.4 eV are shown in the top and middle panels of Fig. 4. There are two general trends. (i) Occupied surface states, which play the role of the initial states in the transitions, tend to be strongly localized on the As dimers. The top As dimers contribute strongly to the s-s transitions, whereas the third-layer dimers are more involved in the s-b signal at 3.4 eV. (ii) Unoccupied surface states, which are the final states in the optical transitions, are mostly localized on the second-layer Ga dangling bonds, although at the higher energy they are more delocalized within the first three layers. The slight oxygen-induced signal *increase* observed at 2.4 eV, which seems at first sight surprising, can also be interpreted using the maps of the surface states responsible for the s-s related signal at the corresponding theoretical energy of 2.9 eV, shown in the bottom panels of Fig. 4. The initial state is localized at the dimer backbonds whereas the final state is localized at the Ga dangling bonds. As a result, this transition is polarized along [110], which explains why the corresponding peak in the s-s spectrum is negative and why its oxygen-induced quenching induces a signal increase.

IV. CONCLUSION

In the present work we show that the peak at 2.95 eV in the RA spectrum of GaAs(001) has a mixed ‘‘surface’’ and ‘‘bulk’’ origin. In the experimental section, we show that the peak position in $Ga_{1-x}In_xAs$ alloys behaves, as a function of x, in the same manner as the bulk optical transition E_1, suggesting a dominant bulk origin. This behavior, as well as the oxygen-induced modifications of the spectrum, is explained using *ab initio* calculations, in which optical transitions are separated according to the surface or bulk nature of the initial and final state of the transition (s-s, s-b, b-s, and b-b). These four components exhibit peaks at the same energy, and the transitions of mixed character (s-b and b-s) contribute to slightly more than half of the peak magnitude. Interpretation of the indium- and oxygen-induced modifications of the optical anisotropy relies on the fact that distinct combinations of the above transitions are relevant for the two cases. While the presence of indium should affect all the transitions, implying a bulk initial or final state, the effect of oxygen strongly suggests that, as expected using electronegativity arguments, oxidation only quenches the transitions for which the initial state is surface related (s-b+s-s).[2,7,8,29] More precise identification of the relative contributions of surface and bulk in the total spectrum is given by the relative spectra of the four above transitions, for which the total sum is in good agreement with the experimental spectrum. The surface states participating in the optical transition are the occupied dimer states and the unoccupied gallium dangling bonds.

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