

Structural fingerprints in the reflectance anisotropy spectra of InP(001)(2×4) surfaces

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The reflectance anisotropy has been calculated from *first principles* for a series of recently proposed structural models of the InP(001)(2×4) surface. The features of the calculated spectra are related to specific surface bonding configurations. We find a pronounced negative anisotropy around 1.7 eV linked to transitions between σ -like In-In bonding states and empty dangling bonds localized at the surface cations. The strength of that anisotropy is directly related to the number of In-In bonds at the surface. This explains the gradual change of the corresponding measured anisotropy in that energy region, depending on the growth conditions. Positive anisotropies at higher energies arise from transitions between P-P dimer related states and surface resonances. Additionally we find derivativelike features at the energy of the E_1 peak that depend only weakly on the surface structure and stoichiometry. In conjunction with the experimental data, our results indicate that the (2×4) reconstructed InP(001) surface features In-In bonds along [110] and P-P dimers parallel to $[1\bar{1}0]$, respectively. The relative number of these bonds varies with the growth conditions. [S0163-1829(99)09003-7]

I. INTRODUCTION

Reflectance anisotropy spectroscopy (RAS), also known as reflectance difference spectroscopy (RDS),¹ has been shown to meet the need for a reliable *in situ* monitoring tool, applicable to ultrahigh vacuum as well as to gas-phase environments.²⁻⁴ Such a tool is particularly useful for materials like InP, which are mainly grown by metal-organic vapor phase epitaxy (MOVPE): Under gas-phase conditions as in MOVPE, electron-based *in situ* techniques cannot be used. RAS takes advantage of the fact that the bulk dielectric responses of cubic materials are essentially isotropic, so any detected anisotropy is necessarily surface-related. The identification of surface phases by RAS is based on the knowledge of RAS “signatures” of specific surface bonding configurations. A theoretical understanding of the relation between surface structural features and the corresponding optical properties thus helps to exploit the potential of RAS.⁵⁻¹²

The structure of the InP(001)(2×4) surface has been subject to a series of recent experimental studies (for a review see, e.g., Ref. 13). In particular, this surface has thoroughly been characterized by means of RAS.¹⁴⁻¹⁹ Its geometry was interpreted in terms of dimerized In and P atoms, based on similarities between the measured reflectance anisotropy (RA) with earlier findings for GaAs(001).²⁰ Other experimental studies, however, claim that the InP surface structure cannot be explained in terms of conventional dimer models: On the grounds of scanning tunneling microscopy (STM) images, Shimomura *et al.*²¹ suggest a structure that combines two In dimers in the third layer with a partial In-P exchange in the uppermost two atomic layers. MacPherson and co-workers²² interpret their STM images in terms of P trimers. A trimerization of the topmost In atoms has seem-

ingly been observed in time-of-flight scattering and recoiling spectrometry.²³

The proposed structural models have recently been probed by *ab initio* total-energy calculations.²⁴ It was found that dimer reconstruction models are energetically the most favored for InP(001)(2×4). The cation-rich surface was suggested to contain mixed In-P dimers on top of an In-terminated surface (cf. Fig. 1). Three P dimers, arranged in the so-called $\beta 2$ geometry,²⁵ form the surface unit cell for more phosphorus-rich conditions. Models with one or two P dimers (top-P-dimer model and α geometry, respectively) may occur for intermediate chemical potentials. All these structures, apart from the $\beta 2$ geometry, are characterized by In-In bonds in the second atomic layer. Very recently, a further surface geometry has been proposed for InP(001): Tsai *et al.*²⁶ suggest a P-tetramer structure derived from the geometry proposed in Ref. 22. We have calculated the total energy of the tetramer structure and found it to be 0.38 eV higher than that of InP(001) α (2×4), which has the same stoichiometry. This energy difference makes the tetramer ge-

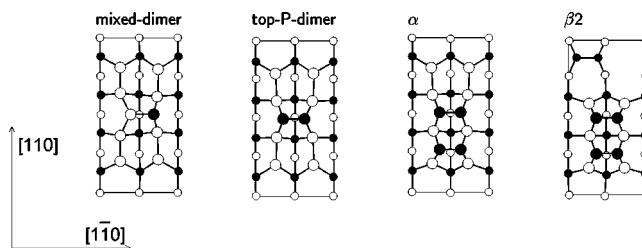


FIG. 1. Top view of energetically favored InP(001)(2×4) surface reconstruction models. Empty (filled) circles represent In (P) atoms. Large (small) symbols indicate positions in the first and second (third and fourth) atomic layers. The reconstructions are ordered by increasing P coverage.

ometry very unlikely to occur.

The aim of the present study is to investigate the surface optical properties of InP(001) and to resolve the controversies regarding its structure by comparison with experiments. For this purpose we calculated the RA of the energetically favored surface structures shown in Fig. 1. The results are compared with measured data and analyzed with respect to the existence and origin of characteristic, surface-bonding related features or ‘‘fingerprints.’’

II. METHOD

The quantity we want to calculate is the anisotropy of the reflectance of polarized light. The general formulas for the reflectance coefficients of s and p radiation have been derived by Del Sole²⁷ from the light-propagation equations at surfaces, taking the inhomogeneity and anisotropy of the surface into account. Polarization-dependent corrections to the Fresnel reflectance appear. Here, we are only interested in the special case of normally incident s waves. As shown by Manghi *et al.*,²⁸ the reflection anisotropy $\Delta R/R$ for light polarized along α and β can be derived from a slab calculation and is given by

$$\frac{\Delta R}{R} := \frac{R_\alpha - R_\beta}{R} = \frac{4\omega d}{c} \operatorname{Im} \left[\frac{4\pi[\alpha_{\alpha\alpha}(\omega) - \alpha_{\beta\beta}(\omega)]}{\epsilon_b(\omega) - 1} \right], \quad (1)$$

where $\epsilon_b(\omega)$ is the bulk dielectric function and $\alpha_{\alpha\alpha}$ and $\alpha_{\beta\beta}$ are components of the optical polarizability tensor of the slab with thickness d . In the following we identify α and β with the $[1\bar{1}0]$ and $[110]$ directions, respectively.

We calculate the slab polarizability in the independent-particle approximation based on the electronic structure obtained within density-functional theory in the local-density approximation (DFT-LDA). Whereas the DFT-LDA method is well established for the study of the atomic structure of semiconductor surfaces, their optical properties are often determined by the empirical tight-binding method.^{5,8,9,12} The main reasons for that are the high cost of *first-principles* calculations of optical properties and the DFT-LDA band-gap problem.²⁹ Our calculations were performed using a recently developed real-space multigrid method.^{30,31} This approach provides for effective convergence acceleration and preconditioning on all length scales. Furthermore, it allows for an efficient parallelization and is thus particularly suitable for large surface reconstructions as studied here.

Top and bottom layers of slab geometries modeling zincblende (001) surfaces have necessarily different bond orientations and thus contribute differently to the optical anisotropy of the slab. This is one of the key problems for the calculations of the RA for III-V(001) surfaces.⁶ The real-space approach employed in our study allows an elegant solution: We use a linear cutoff function¹² in calculating the optical matrix elements and thus suppress the anisotropy of the bottom layer of the slab.

We employ nonlocal norm-conserving pseudopotentials generated according to the scheme by Hamann³² and cast into Kleinman-Bylander form^{33,34} to describe the electron-ion interaction. The In $4d$ electrons are partially taken into account by means of a nonlocal core correction to the exchange and correlation energy. The Perdew-Zunger

parametrization³⁵ of the Ceperley-Alder form³⁶ of the exchange and correlation energy is used. The spacing of the finest grid used to represent the electronic wave functions and charge density in the multigrid real-space approach was determined through a series of InP bulk calculations. We find structural and electronic properties to be converged for a spacing of 0.24 Å. This corresponds to an energy cutoff in plane-wave calculations of about 21 Ry. We calculate a bulk equilibrium lattice constant of 5.84 Å and a bulk modulus of 72.7 GPa (experiment:³⁷ 5.87 Å and 71 GPa). The calculated excitation energies are somewhat smaller than experiment due to the above-mentioned DFT-LDA gap problem. We obtain values of 1.54, 0.89, and 1.59 eV for $E(L_{6c})$, $E(\Gamma_{6c})$, and $E(X_{6c})$. These energies are about 0.2–0.5 eV smaller than those measured in room-temperature (RT) experiments.³⁷ The transition energies $E(\Lambda_{6c} - \Lambda_{4,5,6v})$ and $E(\Gamma_{7c} - \Gamma_{7,8v})$ are underestimated by about 0.7 and 0.6 eV, respectively. Accordingly, the calculated E_1 and E'_0 peaks of the bulk optical spectrum appear around 2.5 and 4.2 eV. Experimentally they are observed at 3.2 and 4.8 eV.³⁸

To model the InP(001) surface we consider a periodic super cell along the surface normal. It contains 12 atomic (001) layers and a vacuum region equivalent in thickness to 8 atomic layers. The dangling bonds at the bottom layer of the slab are saturated with fractionally charged pseudohydrogens.³⁹ It is well known that surface optical spectra strongly depend on geometrical details.^{40,41} Therefore the geometries of the investigated models were carefully relaxed until all calculated forces are below 25 meV/Å. The bottom three layers of the slab were kept frozen in the bulk configuration and the starting coordinates were taken from an earlier plane-wave calculation.⁴² Integrations in the surface Brillouin zone (SBZ) for calculating the atomic and electronic ground state of the surface are performed using four special \mathbf{k} points in the irreducible part. For the calculation of the dielectric function we include all conduction bands within 7.5 eV of the top of the valence bands, using 16 uniformly distributed \mathbf{k} points in the irreducible part of the SBZ. This corresponds to 256 \mathbf{k} points in the full (1×1) SBZ.

III. RESULTS AND DISCUSSION

A. Comparison with experiment

In Fig. 2 we show the RA spectra calculated for the four surface geometries discussed above together with experimental data.^{15,17}

The spectra measured by Ozanyan and co-workers¹⁵ for temperatures between 470 and 590 °C show a distinct temperature dependence: The 590 °C spectrum shows a pronounced negative anisotropy around 1.7 eV, which gradually disappears with decreasing temperature. At the same time the positive anisotropy at 2.6 eV gains strength and the ‘‘three-buckle’’ shape flattens between 3.5 and 4.5 eV, resulting in a ‘‘camelback’’ overall spectrum shape. Reference 15 explains these spectral changes as due to the transition from an In-rich surface to a less In-rich stoichiometry. The assumption of a stoichiometry-related RA is backed by the works of Zorn *et al.*¹⁶ and Postigo and co-workers,¹⁹ who observe similar modifications in their RA spectra measured at varying phosphorus partial pressure. For comparison, we also show a RT

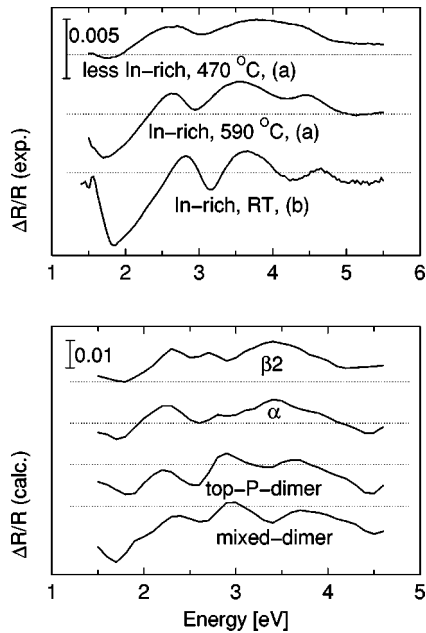


FIG. 2. Upper panel: Measured RA spectra for In-rich and less In-rich InP(001) surfaces from Refs. 15 (a) and 17 (b). Lower panel: RA spectra calculated for the structural models shown in Fig. 1. The zero line in each spectrum is indicated by a horizontal dotted line.

spectrum measured by Kinsky and co-workers¹⁷ at an In-rich InP(001) surface. While the overall line shape is very similar to the corresponding high-temperature spectrum of the In-rich surface, a small blueshift of about 0.1–0.2 eV, together with sharpened and increased anisotropies, occurs. The trend towards enhancement of RA amplitudes holds also for even lower temperatures.⁴³ This should be borne in mind when comparing the measurements with our spectra, calculated at zero temperature.

In the lower panel of Fig. 2 we show the RA calculated for the four structural models shown in Fig. 1. Note the different scale for calculated and measured spectra. We observe a strong negative anisotropy around 1.7 eV for the mixed-dimer model, which contains six In-In bonds along the [110] direction in the surface atomic layer. The strength of this anisotropy is strongly reduced for the top-P-dimer model with four In-In bonds and even weaker in the case of the α structure with two In-In bonds. The $\beta 2$ structure, which does not contain any In-In bonds, shows no negative anisotropy at all. Thus the negative anisotropy below 2 eV seems to be related to the existence of cation-cation bonds. This supports the interpretation of the experimental spectra discussed above and is similar to earlier theoretical findings for the GaAs(001) surface.^{5,12}

The calculated spectra also show a strong dependence on structural details for higher energies. For the $\beta 2$ geometry with three P-P dimers oriented along $[1\bar{1}0]$, we find a relatively broad positive anisotropy between about 2 and 4 eV. Maxima of the anisotropy appear around 2.3 and 3.4 eV and a shoulder exists at 2.7 eV. The shape of that anisotropy is roughly preserved for the α structure, which features two P-P dimers. The magnitude of the anisotropy, however, is somewhat reduced and the spectrum is shifted down. An even further reduction in positive anisotropy between 2 and 4 eV

occurs for the top-P-dimer and mixed-dimer structures, featuring a single P-P or In-P dimer, respectively, on top of an In-terminated substrate. The described evolution of the spectra in the high-energy region shows a correlation between the positive anisotropy and the formation of P-P dimers. Simultaneously with the downshift of the spectrum, also a “three-buckle shape” develops. This closely parallels the evolution of the experimental spectra with increasing In coverage and again resembles earlier theoretical work for GaAs(001).^{5,12}

All structures investigated give rise to a local minimum or derivativelike feature around 2.5 eV, which is only weakly dependent on the structure and stoichiometry of the surface. A similar feature characterizes the measured spectra at an energy of 3.0–3.2 eV. The calculated and measured minima thus coincide with the respective E_1 peaks of the InP bulk optical spectra.

The general line shape of the calculated spectra and in particular the evolution of the spectra with structural changes is in fair agreement with the experimental findings for different growth conditions. The agreement, however, is far from perfect. (i) The calculated anisotropies are about three times larger than measured. This overestimation can be explained partially by the strong temperature dependence of the measurements as discussed above, and the existence of defects and domain boundaries at the sample surface,^{21,22} which can be expected to have a strong effect on the RA.⁴⁴ Furthermore, the calculated surface phase diagram²⁴ suggests a coexistence of different surface geometries for intermediate values of the In chemical potential. The measured spectra may thus present a superposition of different contributions. (ii) Apart from the different peak heights, the energetic positions of the calculated peaks also deviate from experiment. This deviation cannot be remedied by a rigid shift of the conduction bands towards higher energies: The low-energy part of the measured spectra is nearly correctly described, despite the underestimation of the InP bulk excitation energies in the underlying DFT-LDA calculation as discussed in the Introduction. This holds in particular for the strong negative anisotropy around 1.7 eV, which is entirely due to transitions between surface states, as will be shown below. For energies larger than about 2 eV, on the other hand, we observe a distinct redshift in the calculated spectra. Quasiparticle calculations for semiconductor surfaces including many-body effects in the GW approximation^{45–47} have shown that bulk- and surface-state energies may experience different shifts with respect to the eigenvalues of the underlying DFT-LDA calculation. In particular, Hybertsen and Louie⁴⁵ point out that, depending on the orbital character of the specific states, the surface gap may actually open less than the bulk gap, when self-energy effects are included in the calculations. A fortuitous cancellation of self-energy and electron-hole interaction effects⁴⁸ may also contribute to the different shifts of the bulk- and surface-related peaks in the calculated spectra in comparison to the measurements. Unfortunately, both self-energy and electron-hole interaction effects are beyond the scope of the present study.

B. Origin of RA features

We have shown above that the surface atomic structure strongly influences the calculated RA. Moreover, a heuristic correlation between structural units, such as In-In bonds or

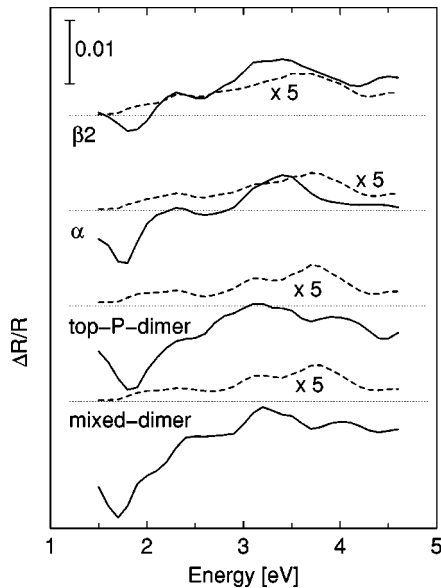


FIG. 3. Calculated RA spectra for InP(001)(2×4) surface structures considering only transitions within (below) the uppermost four atomic layers are shown by solid (dashed) lines. The latter have been scaled by 5. The zero line in each spectrum is indicated by a horizontal dotted line.

P-P dimers, and specific spectral features has been found. Similar findings exist for GaAs(001).¹² This does not explain, however, the origin of the surface RA. In the case of GaAs(001) there is an ongoing discussion: Some authors⁴¹ attribute the RA mainly to electronic transitions between surface-perturbed bulk states. Others assign the features in the calculated RA to particular transitions between pairs of surface states⁵ or to transitions between bulklike states and surface states.⁶ It has also been hypothesized that in many cases RAS line shapes have little to do with the atomic surface structure, but are rather determined by surface-induced changes in the excitonic and local-field effects on bulk transitions.^{49,50}

In order to clarify the origin of the RA in the case of InP, we perform additional calculations. In Fig. 3 we show the calculated RA for the different surface geometries taking into account only transitions within the uppermost four atomic layers. These are the layers where most of the structural and electronic modifications occur, which cause the surface to reconstruct. The calculated spectra are rather similar to those calculated for the complete slab (Fig. 2). This holds in particular for the negative anisotropy around 1.7 eV, which can therefore be attributed to transitions near the surface. The anisotropies at higher energies are also fairly well reproduced by including near-surface transitions only. However, their magnitude is somewhat reduced with respect to the calculation for the full slab. This indicates that surface-modified bulk states do contribute in that energy region. Also shown in Fig. 3 are the parts of the reflectance anisotropy that result from transitions below the uppermost four layers. For all investigated structures these transitions between predominantly bulklike states give rise to a broad and relatively small positive anisotropy with a maximum around 3.7 eV and weak local minima close to the energies of the E_1 and E'_0 peaks of the bulk optical spectrum (at 2.5 and 4.2 eV, respec-

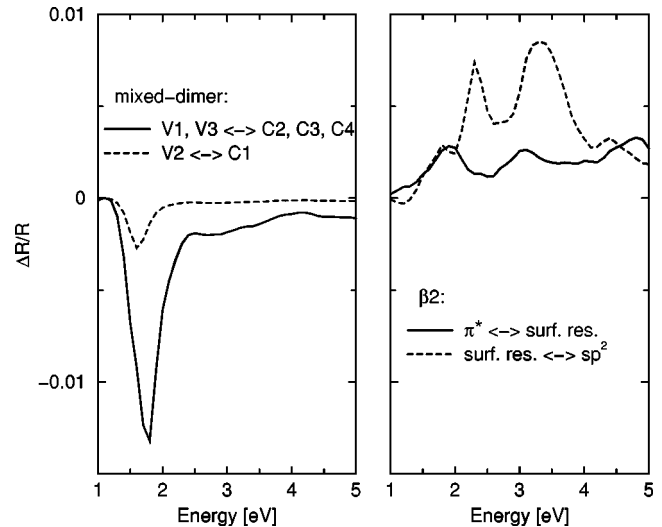


FIG. 4. Calculated RA spectra for the mixed-dimer (left panel) and β_2 structure of the InP(001)(2×4) surface. Only transitions between the indicated electronic states (see text) are considered.

tively). An additional shoulder at 3.1 eV appears in the case of the mixed-dimer and top-P-dimer structures.

A more detailed investigation requires the knowledge of the InP(001) surface band structure. A theoretical analysis of the InP surface bands and the orbital character of the corresponding states has recently been published⁴² and is in agreement with the experimental data available to date.⁵¹ In Fig. 4 we show the calculated RA for the mixed-dimer and β_2 models of the InP(001) surface attributed to transitions between specific states. In the case of the mixed-dimer model we find that the main contribution to the negative anisotropy below 2 eV, which above has been shown to be linked to the existence of In-In bonds, comes indeed from transitions between In-In bonding-related states: Transitions between V1/V3 and C2–C4 (notation from Ref. 42) give rise to a sharp negative peak at 1.8 eV. V1 and V3 are occupied σ -like In-In bonding states close to the bulk valence-band maximum (VBM) of InP. Their orbital characters are shown in Fig. 5. These are bound surface states around the K point of the SBZ.⁴² C2–C4 are empty dangling bonds localized at threefold-coordinated surface cations (cf. Fig. 5). Their energetical positions are within the upper part of the projected bulk band gap. Transitions between V1/V3 and C2–C4 account for about two-thirds of the negative anisotropy in the low-energy region. A smaller contribution around 1.6 eV is due to transitions between V2 and C1. V2 corresponds to a lone pair of electrons at the topmost P atom, energetically slightly below the bulk VBM. The lowest unoccupied surface state, C1, contains contributions from empty In dangling bonds and an antibonding π^* combination of In-P dimer states. States comparable to V1 and V3 and C2–C4, both in energetical position and orbital character, are also found at the In-In bonds of the top-P-dimer model and the α structure of the InP(001) surface. This explains the strong correlation between the number of these bonds and the calculated (and measured) RA below 2 eV, as demonstrated above. Similar states also exist at In-In bonds of In-covered GaAs(001) surfaces,⁵² Ga-Ga dimers of (4×2)-reconstructed GaAs(001) surfaces,⁵³ and Ga-Ga bonds of Sb-covered

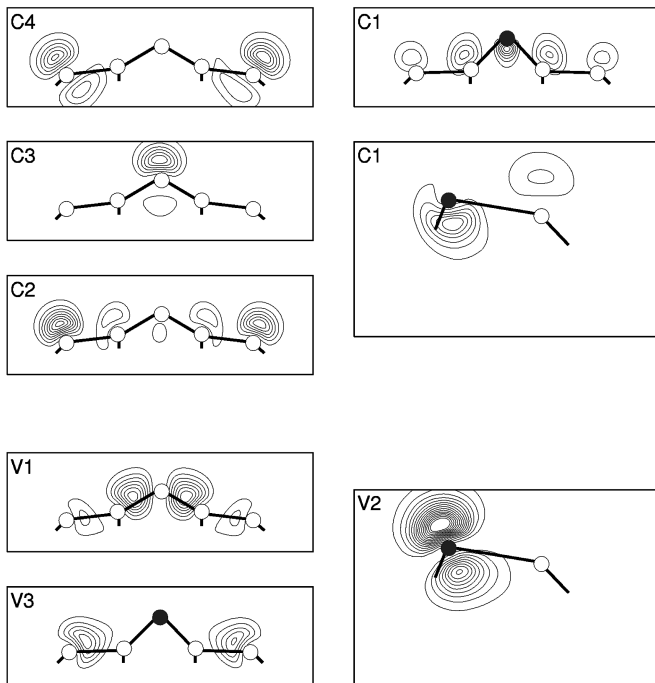


FIG. 5. Contour plots of the squared wave functions at K for surface localized states of the mixed-dimer model of the $\text{InP}(001)(2 \times 4)$ surface. The contour spacing is $7.5 \times 10^{-4} e/\text{Bohr}^3$. The wave functions are plotted in $(1\bar{1}0)$ and (110) planes, containing the second-layer cation-cation bonds and the In-P dimer, respectively.

$\text{GaAs}(001)$ surfaces.⁵⁴ In all these cases a strong negative RA around 2 eV has been observed experimentally.^{55,20,9} There exists thus a strong correlation between structural units such as cation-cation bonds and specific line shapes even for chemically different systems. However, a word of caution is in order. Pronounced cation-cation bonds also occur at the $\text{GaAs}(001)\alpha(2 \times 4)$ surface. The cation-derived surface states are, however, resonant with the projected bulk states.⁵⁶ Accordingly, no, or only comparatively little, negative anisotropy appears in the corresponding RA spectrum.^{12,20}

P-P dimers in $\beta 2$ or α geometries give rise to a relatively broad positive anisotropy with calculated maxima around 2.3 and 3.4 eV, as shown above. This anisotropy obviously cannot be due to transitions between bound surface states only. In Fig. 4 we show that transitions between bound surface states and surface resonances play a decisive role in the case of the $\text{InP}(001)\beta 2(2 \times 4)$ surface: Transitions between occupied antibonding π^* combinations of P-P dimer states, which lie slightly below the bulk VBM and are bound around the K point of the SBZ,⁴² and unoccupied surface resonances cause a broad positive anisotropy over the full energy range. Strong positive RA features at 2.3 and 3.4 eV arise from transitions between occupied surface resonances and empty sp^2 orbitals localized at the threefold coordinated

surface cations bonded to the P-P dimers. Such states are typical for α and $\beta/\beta 2$ structures of III-V(001) surfaces.^{42,56} They are mainly responsible for the appearance of the ‘‘camelback’’ spectrum shape associated with the existence of anion dimers. The single P-P dimer of the top-P-dimer model and the In-P dimer of the mixed-dimer structure are not bonded to threefold-coordinated cations (cf. Fig. 1). Accordingly, no, or only little positive anisotropy shows up in their RA spectra.

Our assignments of specific features in the RA spectra to transitions involving characteristic surface states agree with earlier tight-binding findings for $\text{GaAs}(001)$.⁵ The agreement may, however, be somewhat fortuitous: The tight-binding calculations modelled the surface geometry by dimers arranged in (1×2) units. Thus the electron counting rule was violated and the surface geometry could only be approximated.

The contribution of surface states to the calculated RA seems to be larger for $\text{InP}(001)$ than recently found for $\text{GaAs}(001)$.⁴¹ This can at least partially be explained by the differences between the surface band structures of $\text{InP}(001)$ (Ref. 42) and $\text{GaAs}(001)$.⁵⁶ In particular, the density of unoccupied surface states in the region of the projected bulk band gap is much higher in InP . This difference is in turn related to the larger size of the In atoms, leading to a reduced energy splitting between bonding and antibonding orbital combinations.

IV. SUMMARY

We calculated the reflectance anisotropy spectra for energetically favored structural models for the $\text{InP}(001)(2 \times 4)$ surface. Our results compare reasonably with experiment if one considers that many-body effects beyond the DFT-LDA are neglected and that the calculations are restricted to ideal surfaces at zero temperature. The calculated spectra support the existence of different surface structures, dominated by In-In bonds along $[110]$ and In-P or P-P dimers parallel to $[1\bar{1}0]$, depending on the particular experimental conditions. We find that surface states related to structural units, such as cation-cation bonds, threefold-coordinated surface cations, and anion-anion dimers, give rise to characteristic fingerprints in the reflectance anisotropy. As shown by comparison to $\text{GaAs}(001)$, however, these fingerprints are not necessarily universal and have to be established for the investigated material.

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¹D. E. Aspnes and A. A. Studna, Phys. Rev. Lett. **54**, 1956 (1985).

²D. E. Aspnes, Surf. Sci. **307-309**, 1017 (1994).

³W. Richter and J. T. Zettler, Appl. Surf. Sci. **101**, 465 (1996).

⁴*Epioptics. Linear and Nonlinear Optical Spectroscopy of Surfaces and Interfaces*, edited by J. F. McGilp, D. Weaire, and C. H. Patterson (Springer-Verlag, Berlin, 1995).

- ⁵D. E. Aspnes, Y. C. Chang, A. A. Studna, L. T. Florez, H. H. Farrell, and J. P. Harbison, *Phys. Rev. Lett.* **64**, 192 (1990); Y. C. Chang and D. E. Aspnes, *Phys. Rev. B* **41**, 12 002 (1990).
- ⁶S. J. Morris, J. M. Bass, and C. C. Matthai, *Phys. Rev. B* **52**, 16 739 (1995).
- ⁷L. Kipp, D. K. Biegelsen, J. E. Northrup, L.-E. Swartz, and R. D. Bringans, *Phys. Rev. Lett.* **76**, 2810 (1996).
- ⁸P. V. Santos, B. Koopmans, N. Esser, W. G. Schmidt, and F. Bechstedt, *Phys. Rev. Lett.* **77**, 759 (1996).
- ⁹N. Esser, A. I. Shkrebtii, U. Resch-Esser, C. Springer, W. Richter, W. G. Schmidt, F. Bechstedt, and R. Del Sole, *Phys. Rev. Lett.* **77**, 4402 (1996).
- ¹⁰V. I. Gavrilenko and F. Bechstedt, *Phys. Rev. B* **56**, 3903 (1997).
- ¹¹Z. Sobiesierski, D. I. Westwood, and C. C. Matthai, *J. Phys.: Condens. Matter* **10**, 1 (1998).
- ¹²A. I. Shkrebtii, N. Esser, W. Richter, W. G. Schmidt, F. Bechstedt, B. O. Fimland, A. Kley, and R. Del Sole, *Phys. Rev. Lett.* **81**, 721 (1998).
- ¹³Q.-K. Xue, T. Hashizume, and T. Sakurai, *Prog. Surf. Sci.* **56**, 1 (1997), and references therein.
- ¹⁴D. Pahlke, J. Kinsky, Ch. Schultz, M. Pristovsek, M. Zorn, N. Esser, and W. Richter, *Phys. Rev. B* **56**, R1661 (1997).
- ¹⁵K. B. Ozanyan, P. J. Parbrook, M. Hopkinson, C. R. Whitehouse, Z. Sobiesierski, and D. I. Westwood, *J. Appl. Phys.* **82**, 474 (1997).
- ¹⁶M. Zorn, T. Trepk, J.-T. Zettler, B. Junno, C. Meyne, K. Knorr, T. Wethkamp, M. Klein, M. Müller, W. Richter, and L. Samuelson, *Appl. Phys. A: Mater. Sci. Process.* **65**, 333 (1997).
- ¹⁷J. Kinsky, Ch. Schultz, D. Pahlke, A. M. Frisch, T. Herrmann, N. Esser, and W. Richter, *Appl. Surf. Sci.* **123**, 228 (1998).
- ¹⁸T. K. Johal, S. D. Barrett, M. Hopkinson, P. Weightman, and J. R. Power, *J. Appl. Phys.* **83**, 480 (1998).
- ¹⁹P. A. Postigo, G. Armelles, T. Utzmeier, and F. Briones, *Phys. Rev. B* **57**, 1362 (1998).
- ²⁰I. Kamiya, D. E. Aspnes, L. T. Florez, and J. P. Harbison, *Phys. Rev. B* **46**, 15 894 (1992).
- ²¹M. Shimomura, N. Sanada, Y. Fukuda, and P. J. Møller, *Surf. Sci.* **359**, L451 (1996).
- ²²C. D. MacPherson, R. A. Wolkow, C. E. J. Mitchell, and A. B. McLean, *Phys. Rev. Lett.* **77**, 691 (1996).
- ²³M. M. Sung, C. Kim, H. Bu, D. S. Karpuzov, and J. W. Rabalais, *Surf. Sci.* **322**, 116 (1995).
- ²⁴W. G. Schmidt, F. Bechstedt, N. Esser, M. Pristovsek, Ch. Schultz, and W. Richter, *Phys. Rev. B* **57**, 14 596 (1998).
- ²⁵J. E. Northrup and S. Froyen, *Phys. Rev. B* **50**, 2015 (1994).
- ²⁶M.-H. Tsai, C. F. Liu, and L.-K. Hsu, *Bull. Am. Phys. Soc.* **43**, 862 (1998).
- ²⁷R. Del Sole, *Solid State Commun.* **37**, 537 (1981).
- ²⁸F. Manghi, R. Del Sole, A. Selloni, and E. Molinari, *Phys. Rev. B* **41**, 9935 (1990).
- ²⁹F. Bechstedt, in *Festkörperprobleme/Advances in Solid State Physics*, edited by U. Rössler (Vieweg, Braunschweig, 1992), Vol. 32, p. 161.
- ³⁰E. L. Briggs, D. J. Sullivan, and J. Bernholc, *Phys. Rev. B* **52**, R5471 (1995).
- ³¹E. L. Briggs, D. J. Sullivan, and J. Bernholc, *Phys. Rev. B* **54**, 14 362 (1996).
- ³²D. R. Hamann, *Phys. Rev. B* **40**, 2980 (1989).
- ³³L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ³⁴M. Fuchs and M. Scheffler, *Comput. Phys. Commun.* (to be published).
- ³⁵J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ³⁶D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ³⁷*Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a and Vol. 22, Pt. a III/22a (Springer-Verlag, Berlin, 1982).
- ³⁸P. Lautenschlager, M. Garriga, and M. Cardona, *Phys. Rev. B* **36**, 4813 (1987).
- ³⁹K. Shiraiishi, *J. Phys. Soc. Jpn.* **59**, 3455 (1990).
- ⁴⁰C. Kress, A. I. Shkrebtii, and R. Del Sole, *Surf. Sci.* **377-379**, 398 (1997).
- ⁴¹R. Eryiğit and I. P. Herman, *Phys. Rev. B* **56**, 9263 (1997).
- ⁴²W. G. Schmidt and F. Bechstedt, *Surf. Sci.* **409**, 474 (1998).
- ⁴³V. L. Berkovits, I. V. Makarenko, T. A. Minashvili, and V. I. Safarov, *Solid State Commun.* **56**, 449 (1985).
- ⁴⁴B. S. Mendoza, R. Del Sole, and A. I. Shkrebtii, *Phys. Rev. B* **57**, R12 709 (1998).
- ⁴⁵M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **38**, 4033 (1988).
- ⁴⁶F. Bechstedt and R. Del Sole, *Solid State Commun.* **74**, 41 (1990).
- ⁴⁷C. Kress, M. Fiedler, W. G. Schmidt, and F. Bechstedt, *Phys. Rev. B* **50**, 17 697 (1994).
- ⁴⁸M. Rohlfing and S. G. Louie, *Phys. Rev. Lett.* **80**, 3320 (1998); S. Albrecht, L. Reining, R. Del Sole, and G. Onida, *ibid.* **80**, 4510 (1998); L. X. Benedict, E. L. Shirley, and R. B. Bohn, *ibid.* **80**, 4514 (1998).
- ⁴⁹U. Rossow, L. Mantese, and D. E. Aspnes, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1997), p. 831.
- ⁵⁰K. Uwai and N. Kobayashi, *Phys. Rev. Lett.* **78**, 959 (1997).
- ⁵¹W. R. A. Huff, M. Shimomura, N. Sanada, G. Kaneda, T. Takeuchi, Y. Suzuki, H. W. Yeom, T. Abukawa, S. Kono, and Y. Fukuda, *J. Electron Spectrosc. Relat. Phenom.* **88-91**, 609 (1998); *Phys. Rev. B* **57**, 10 132 (1998); further refs. can be found in Ref. 42.
- ⁵²W. G. Schmidt, P. Käckell, and F. Bechstedt, *Appl. Surf. Sci.* **123**, 136 (1998).
- ⁵³W. G. Schmidt, *Appl. Phys. A: Mater. Sci. Process.* **65**, 581 (1997).
- ⁵⁴W. G. Schmidt and F. Bechstedt, *Phys. Rev. B* **55**, 13 051 (1997).
- ⁵⁵C. Springer, U. Resch-Esser, C. Golletti, W. Richter, and B. O. Fimland, *Surf. Sci.* **377-379**, 404 (1997).
- ⁵⁶W. G. Schmidt and F. Bechstedt, *Phys. Rev. B* **54**, 16 742 (1996).