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Theoretical Aspects of the Optical Response of Semiconductor Surfaces

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We discuss the progress in realistic calculations of the optical response of semiconductor surfaces. It concerns numerical developments as well as the better inclusion of many-body effects. We show that the starting point of such calculations, the atomic structure and the surface equilibrium phase, can be now derived with high accuracy. The different steps are described in detail for the computation of the reflectance anisotropy and the exploration of the In-rich InP(001)2 × 4 surfaces.

1. Introduction

Surface reflectance spectroscopies in the visible to near-UV spectral range have successfully been used for monitoring surfaces during film growth by molecular beam epitaxy (MBE) and metallorganic vapour phase epitaxy (MOVPE) as well as for exploring surface geometries belonging to a certain translational symmetry [1]. These surface sensitive techniques include spectroscopic ellipsometry, reflectance difference spectroscopy and surface photoabsorption [2].

One frequently used method is the reflectance anisotropy spectroscopy (RAS), schematically described in Fig. 1 for normal incidence. It measures the difference in the reflection $R_{x/y}(\omega)$ for light of two orthogonal polarizations x and y , normally incident on a surface, as a function of the photon energy $\hbar\omega$. When light is reflected in normal incidence from a cubic crystal, its intensity cannot be dependent on its polarization. The small measured relative difference²⁾

$$\frac{\Delta R(\omega)}{R(\omega)} = 2 \frac{R_x(\omega) - R_y(\omega)}{R_x(\omega) + R_y(\omega)} \quad (1)$$

is a consequence of the anisotropy of the illuminated crystal surface.

The spectral dependence of the RAS can be used to explore the surface atomic structure [3]. However, this requires a careful theoretical modelling of the surface considered [4]. In principle, the surface structure can be identified by comparison between

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²⁾ Frequently the surface signal is given by the complex reflectances and only the real part of the corresponding ratio is plotted. In these cases we write $\Delta r/r$ instead of Equ. (1).

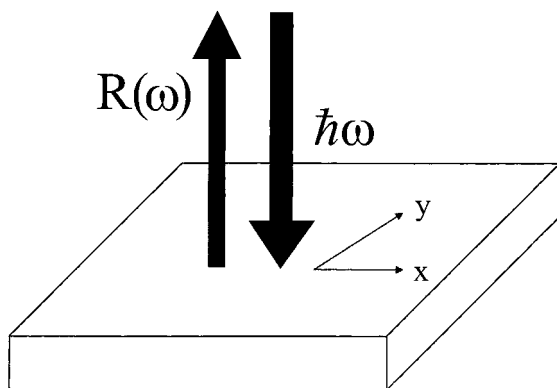


Fig. 1. Schematic representation of the reflectance anisotropy spectroscopy

theoretical spectra for hypothesized test structures and the experimental one as shown schematically in Fig. 2.

For given translational symmetry the experimental and theoretical facts known about such a surface may be used (i) to develop a certain structural model. In a second step (ii), for this model the exact atomic coordinates are derived by minimizing the total energy. This is usually accompanied by selecting the energetically most favourable surface phase (here: model) for a given stoichiometry. It follows (iii) the determination of the corresponding electronic structure including many-body effects in order to describe the excitation aspect. Finally, (iv) an RA spectrum is calculated, which is compared

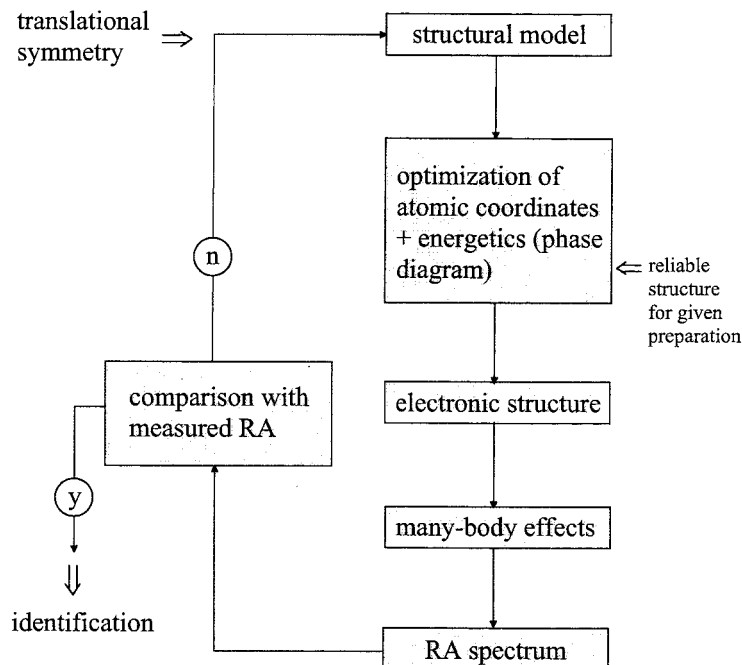


Fig. 2. Block diagram of the cycle for identifying a surface geometry by comparison of theoretical and experimental RA spectra

with the measured spectrum. The procedure can be finished in this last step (v) when agreement is observed (y). Otherwise (n), the procedure has to be repeated until agreement is found. For several clean and adsorbate-covered (110) and (001) surfaces of InP and GaAs we have recently demonstrated that the surface structure can indeed be determined using the approach described above [5 to 15].

In this paper, the progress in performing the five steps should be discussed in more detail. We begin with a brief review of the standard methods to calculate the RAS in Section 2. A demonstration of the progress follows in Section 3. We discuss it with respect to computational aspects, the inclusion of many-body effects and the calculation of surface phase diagrams. An example of a surface exploration is also given. Finally, a brief summary follows in Section 4.

2. Method

Theoretical work on the RAS has progressed along three different approaches. (i) Mochrán and Barrera [16] identified local field effects as being responsible for the observed surface anisotropy. In contrast to an earlier work [3] (ii) Aspnes and coworkers [17] favour modifications of bulk optical transitions as origin of RA spectra. The third approach (iii) starts from the full electronic structure of the combined surface/bulk system. The first calculations by Selloni et al. [18] were performed within a single-particle picture in which the electronic eigenstates were calculated explicitly and the optical functions derived summing up all electronic transitions. Subsequent work has been done within all pictures, for instance in Refs. [19, 20] (i) and Refs. [21, 22] (ii). RA spectra calculated within the third approach usually show a reasonable agreement with experiment [8, 11, 14, 15, 23 to 30], suggesting this to be appropriate when dealing at least with semiconductor surfaces. We therefore follow this line throughout the present paper.

The total-energy and electronic-structure calculations for surfaces are usually performed within the repeated-slab approximation [31]. One example for such slabs used for polar (001) surfaces of III–V compounds is shown in Fig. 3. Modelling the semi-infinite solid within the repeated-slab approximation, the RA spectra (1) can be calculated for normally incident light by [4, 23, 32, 33]

$$\frac{\Delta R(\omega)}{R(\omega)} = \frac{16\pi d\omega}{c} \operatorname{Im} \frac{\alpha_{xx}^{\text{hs}}(\omega) - \alpha_{yy}^{\text{hs}}(\omega)}{\varepsilon_b(\omega) - 1}, \quad (2)$$

where $\varepsilon_b(\omega)$ is the bulk dielectric function.

The half-slab polarizability (more strictly its imaginary part) can be represented within the single-particle approximation as ($i = x, y$) [23]

$$\operatorname{Im} \alpha_{ii}^{\text{hs}}(\omega) = \frac{1}{4d} \sum_{c,v} \int_{2\text{DBZ}} d^2\mathbf{k} F_{cv}^i(\mathbf{k}, \omega), \quad (3)$$

where d is half of the slab thickness and

$$F_{cv}^i(\mathbf{k}, \omega) = \frac{e^2}{m\omega^2\pi} |\langle c\mathbf{k} | p_i | v\mathbf{k} \rangle|^2 \delta(\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k}) - \hbar\omega). \quad (4)$$

Local-field effects due to the atomic structure of matter have been neglected. Another assumption concerns the locality of the single-particle potential. Otherwise a more gen-

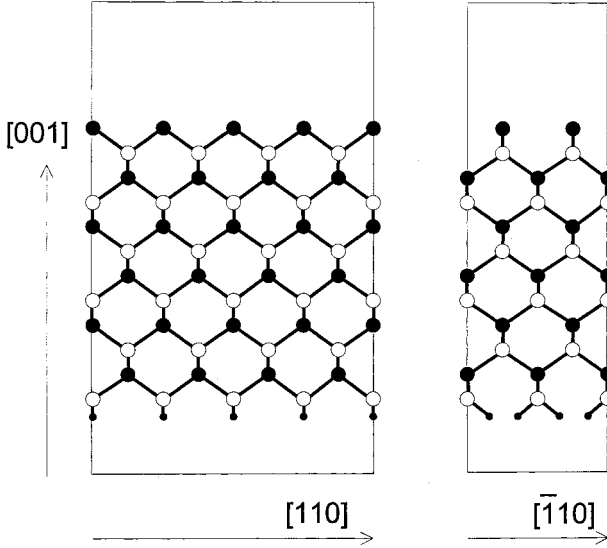


Fig. 3. Side views of the slabs used in the repeated slab calculations for polar (001) surfaces of III-V compounds. The lower side is saturated by pseudohydrogen

eral transition operator than the momentum one has to be taken into account [34, 29]. The bulk dielectric function occurring in Equ. (2) can be computed using an expression similar to that in Equ. (3).

Our calculations are based on density-functional theory (DFT) in local density approximation (LDA). Explicitly, a pseudopotential plane-wave method [35] or pseudopotentials together with a real-space multigrid method [36] are applied. The artificial periodic slab geometries consist of atomic slabs with 10 atomic (110) layers or 12 atomic (001) layers. In the latter case the cation-terminated bottom layer of each slab is saturated with fractionally charged hydrogen atoms. The minima of the total-energy functional with respect to both the atomic and electronic degrees of freedom are determined. The atoms are assumed to be in their fully relaxed positions when the forces acting on the ions are smaller than $0.025 \text{ eV/\AA}$. For the optical calculations the theoretical atomic structures are used. The wave functions $|n\mathbf{k}\rangle$ and the eigenvalues $\varepsilon_n(\mathbf{k})$ ($n = c, v$) resulting from the Kohn-Sham equations of the DFT-LDA are used as a first approximation to the electronic structure of the system. The $\mathbf{k}$ -space integration is usually replaced by a few number of special points, at least within the total energy calculations. Computing the slab polarizabilities more special points are taken into account. For instance, in the case of (001) 2×4 surfaces we use 16 $\mathbf{k}$ -points distributed uniformly in the irreducible part of the two-dimensional (2D) surface Brillouin zone (BZ).

3. Progress

3.1 Computational developments

3.1.1 Triangle method

One numerical problem in the computation of the half-slab polarizability (3) concerns the integration over the Dirac's δ -functions in expression (4). In order to perform this

integration efficiently, the linear-analytic tetrahedron method of the BZ integration [37] has been developed for bulk systems. This line of developments can be also followed in the 2D case [8, 38]. The basic idea is to divide the 2DBZ into triangles and to calculate the integral over the whole BZ as a sum of integrals over each triangle. The energies and matrix elements can be interpolated along the edges of a triangle. This allows to perform the integration analytically. It holds for each triangle in expression (3)

$$\int_{\text{triangle}} d^2\mathbf{k} F_{\text{cv}}^i(\mathbf{k}, \omega) = \int dE_{\text{cv}} \int_{L(E_{\text{cv}})} dl \frac{F_{\text{cv}}^i(\mathbf{k}, \omega)}{|\nabla_{\mathbf{k}} E_{\text{cv}}(\mathbf{k})|}, \quad (5)$$

where one line integration has been to be performed along the line segment $L(E_{\text{cv}})$ in the triangle on which the interband energy is constant and equal to E_{cv} . Then the energy integration in expression (5) can be analytically performed by means of the δ -function in expression (4) for $F_{\text{cv}}^i(\mathbf{k}, \omega)$. Results are given in Fig. 4 for different numbers $N_{\mathbf{k}}$ of $\mathbf{k}$ -points in the irreducible part of the BZ. The results of the triangle method are compared with those obtained using special points according to Monkhorst and Pack [39]. As a model surface the cleavage (110) 1×1 face of InP is considered. There is a clear tendency to converge to the same spectral lineshape of the RA for a huge number of $\mathbf{k}$ -points, at least in the photon energy region below 4.4 eV. However, in the case of the triangle method this convergence is

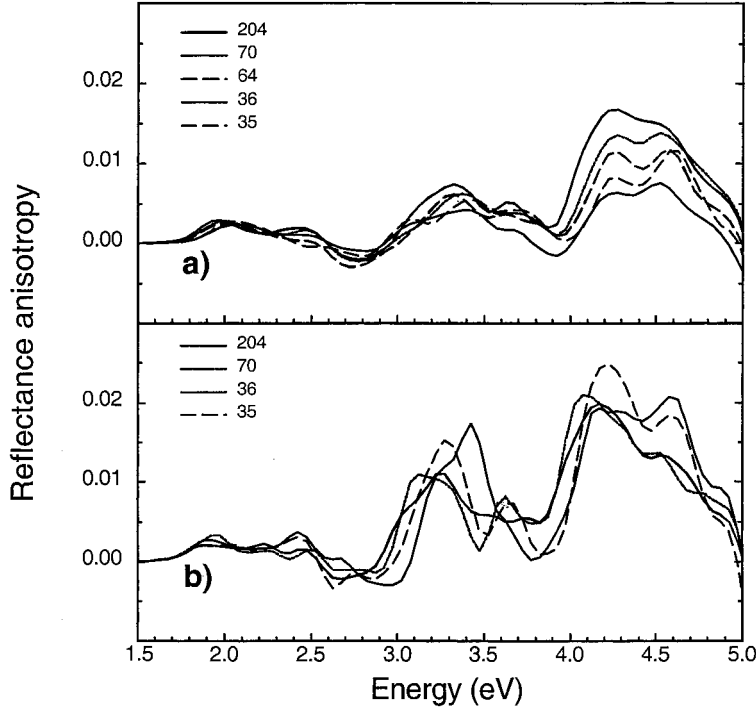


Fig. 4. Reflectance anisotropy spectrum of InP(110) 1×1 , a) using the triangle method and b) using the special-point method together with sets of Monkhorst-Pack points. $x = [\bar{1}10]$ and $y = [001]$ are chosen

much faster and also more regular. Already for a few number of points, e.g. 35, reasonable convergence is reached as far as the $\mathbf{k}$ -points are roughly homogeneously distributed over the 2DBZ.

3.1.2 Real-space treatment

A further computational simplification, in particular for polar surfaces, is realized by the exploitation of the real-space representation of the electronic wave functions within the real-space multigrid method [36]. The repeated-slab description of polar surfaces requires the saturation of the dangling bonds on one slab side by pseudohydrogen to avoid artificial charge transfer. Top and bottom layers of the slab geometries modelling zinc-blende (001) surfaces have necessarily different chemical nature and orientation of the bonds and, thus, contribute differently to the optical anisotropy of the slab. This is one of the key problems for the calculation of the RA for III–V (001) surfaces. In the case of the calculation of the slab polarizability (3) we have to prevent an artificial optical anisotropy due to this pseudohydrogen-covered surface. We have to subtract the effect of this slab side. The easiest method is to introduce a Θ function to real space to cut the lower slab part. However, this gives rise to a nonlocal optical transition operator in $\mathbf{k}$ -space and, hence, can be only used in the plane-wave scheme with a huge numerical effort. On the other hand, the real-space approach employed in our studies

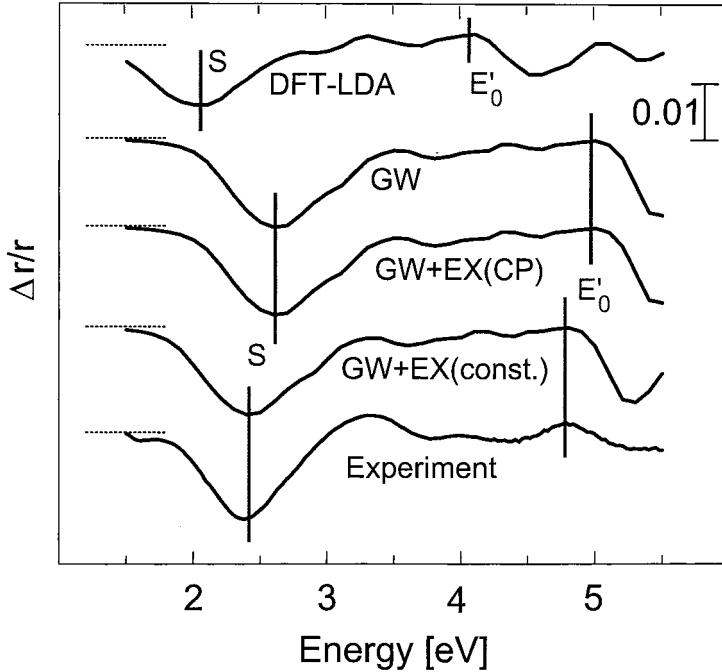


Fig. 5. RA spectra for GaP(001) 2×4 surface. The calculations have been done within the DFT-LDA, adding quasiparticle corrections in GW approximation or taking excitonic effects (EX) into account using the contact-potential approximation (CP) or a constant electron-hole interaction (const). Prominent surface (S) and bulk-related (E'_0) features are highlighted. The measured spectrum is taken from Ref. [40]

allows an elegant solution. A linear cut-off function is introduced in the calculation of the optical matrix elements [11] and thus suppresses the anisotropy of the bottom layers of each slab.

In the case of the polar (001) 2×4 surfaces the wave functions, electron density and single-particle potentials are directly represented on a uniform orthorhombic real-space grid with a certain linear spacing. The linear function to cut the influence of the pseudohydrogen depends only on the z coordinate. The momentum operator is described numerically by a six-point scheme with points in a distance of about 0.24 Å for the phosphides. The space integration is represented by a summation. The corresponding calculations of the optical matrix elements and the diagonalization of the Kohn-Sham equations can be efficiently parallelized and, thus, are suitable for large reconstructions as studied here. A result is presented for the GaP(001) 2×4 surface in Fig. 5. Only the so-called mixed dimer model [13] (cf. Fig. 6) is considered for this Ga-rich surface. A mixed Ga–P dimer is deposited on top of a complete Ga(001) layer. The x and y coordinates are identified with the $[1\bar{1}0]$ and $[110]$ directions. The lineshape resulting for the reflectance anisotropy within DFT-LDA agrees already reasonably with the corresponding experimental spectrum [40]. This holds in particular for the significant negative anisotropy in the low-energy range (denoted S in Fig. 5). This feature is mainly related to optical transitions between filled Ga–Ga bonding states and empty dangling bond states located at surface Ga atoms. Its energetical position is underestimated in the DFT-LDA calculation by about 0.3 eV with respect to the measured spectrum [40]. A much stronger underestimation of about 0.7 eV occurs for the essentially bulk-related features at higher photon energies, as indicated by the maximum observed at the position of the E'_0 critical point in Fig. 5. The main difference between the two spectra concerns a rigid shift of about 0.4 eV.

3.2 Many-body effects

3.2.1 Quasiparticle shifts

Peak energies in excitation spectra can be significantly different from those constructed with the solutions of the Kohn-Sham equations of the DFT-LDA (cf. Fig. 5). Their accurate description requires a rigorous treatment within a Green's function method [41]. The difference between the exchange-correlation self-energy Σ and the corresponding potential index used within the DFT-LDA shifts the excitation energies. Usually, in Hedin's GW approximation [41] Σ is linearly expanded into the dynamically screened Coulomb interaction W . The corresponding quasiparticle shift $\Delta_n(\mathbf{k})$ of a band state $\varepsilon_n(\mathbf{k})$ is then calculated in first-order perturbation theory. It results in complete quasiparticle band structures.

For bulk systems quasiparticle calculations are now standard [42]. Meanwhile such calculations are also performed for semiconductor surfaces [27, 43 to 46]. However, the effort is considerable, and becomes almost prohibitive when calculating surface optical properties, since many $\mathbf{k}$ -points are needed. To solve the dilemma concerning the number of mesh points and effort, the accuracy of the self-energy calculations can be reduced [47, 48]. In addition to the charge density, a model dielectric function of the material is required, which makes the application of that approach to surfaces problematic. In Refs. [49, 50] it has been shown, however, that the final band structure does

not depend very much on the actual value of the dielectric constant, neither for bulk systems nor for surfaces. The RA spectrum for GaP(001) 2×4 taking into account the quasiparticle shifts according to Refs. [49, 50] is also presented in Fig. 5. The most important effect of the quasiparticle corrections is a non-uniform shift of the spectrum towards higher photon energies. We observe a stronger shift for the bulk-related features than for the surface signatures. In addition we find small changes in the lineshape. The shoulder at about 2.8 eV in the DFT-LDA spectrum develops into a local maximum at about 3.5 eV, in reasonable agreement with experiment. It seems that the approximate treatment of the quasiparticle effects tends to overestimate slightly the accompanying shifts.

Presently we are working on a more accurate, but still numerically efficient method to account for local-field effects and dynamical screening at the surface. Work is also in progress to overcome the restriction to first-order perturbation theory in the calculation of the self-energy [51].

3.2.2 Electron–hole interaction

In the last year there was a substantial progress in the treatment of excitonic effects in optical spectra of bulk semiconductors [52 to 54]. This seems to be continued for surfaces, as recently demonstrated for the Si(111) 2×1 surface [55]. However, a complete inclusion of the electron–hole interaction in the calculation of RA spectra remains rather computer-time consuming. For that reason we discuss two extreme approximations of the interaction within an electron–hole pair. We study (i) the contact-potential approximation where the attractive interaction is nearly described by a Dirac’s δ -function. The second approximation (ii) makes such an assumption in $\mathbf{k}$ -space. In other words, the electron–hole interaction is replaced by a certain constant independent of the band indices and the wave vectors. The constant is adjusted.

The effect of both approximations is also demonstrated in Fig. 5. Despite of the strong influence of the electron–hole interaction on each individual optical transition in the contact-potential approximation, the net effect goes to zero due to the strong destructive interference of the contributions from different optical transitions. On the other hand, the other extreme limit of the treatment of excitonic effects, the constant electron–hole interaction, gives rise to a shift to lower energies by the average excitonic binding energy. The lineshape of the RA spectrum remains practically unchanged. For photon energies below 4.8 eV an excellent agreement between theoretical and measured reflectance anisotropy is observed.

3.3 Structure exploration: In-rich InP(001) 2×4 surfaces

3.3.1 Energetics and other facts

We probed a variety of structural models proposed for the InP(001) 2×4 and 4×2 surfaces. In addition to the eleven test structures considered recently [13], we have also studied the so-called $\delta(2 \times 4)$ surface structure (cf. Fig. 6), which is believed to describe the Sb-induced GaAs(001) 2×4 reconstruction [56]. For the most In-rich surfaces we predict the formation of mixed In-P dimers on top of an In-terminated surface (cf. Fig. 6). This structure explains the experimental findings of the core-level photoemission spectroscopy [12]: One P2p versus two In4d surface components reflect the singular P-surface site versus two distinct In-surface sites (three- and fourfold coordination). Three P dimers in the so-called $\beta 2$ geometry form the surface unit cell for less In-rich conditions. The δ -structure

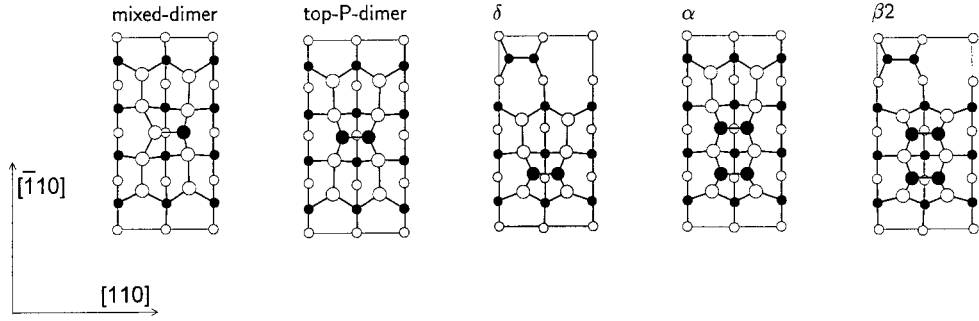


Fig. 6. Top view of energetically favoured cation-rich InP and GaP(001) 2×4 surface reconstruction models. Empty (filled) circles represent cations (P atoms). Large (small) symbols indicate positions in the first and second (third and fourth) atomic layers. The models are ordered with respect to the surface stoichiometry

(cf. Fig. 6) with one P dimer and missing In atoms may occur for intermediate chemical potentials. However, models with one or two P dimers on top of a complete In layer (top-P-dimer model and α geometry, respectively) cannot be completely excluded. They are close in energy to the δ -structure. An explanation for the energetical preference of isolated dimers for InP surfaces (in contrast to GaAs(001)) is the relatively low subsurface strain, while at the same time the electron counting rule can be fulfilled. Because of the size difference in the In and P atoms strain effects play a more important role as in the case of GaAs(001) surfaces with atoms of nearly the same covalent radius. Meanwhile, we have also performed structural optimizations for more P-rich surfaces using $c(2 \times 2)$, $p(2 \times 2)$, $c(4 \times 2)$, and $c(4 \times 4)$ translational symmetries [57]. These calculations clearly

indicate the stability of the mixed-dimer reconstruction under In-rich conditions. For less In-rich preparation conditions the realization of the other models in Fig. 6 becomes unfavourable, however, cannot be excluded because of similar energies.

3.3.2 RA spectra as a tool

In order to clarify the situation we have calculated the RA spectra for the five reconstructions shown in Fig. 6. The results obtained within DFT-LDA are presented in Fig. 7. With the decrease of the In con-

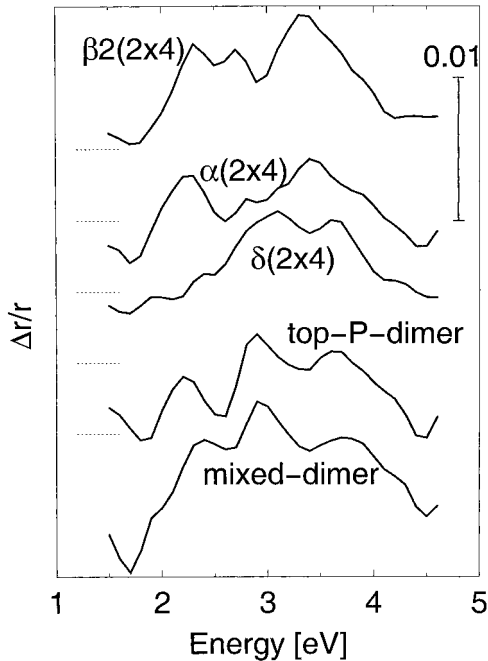


Fig. 7. Calculated RA spectra of favourable InP surface structures. Light polarizations parallel $x \parallel [110]$ and $y \parallel [110]$ are considered

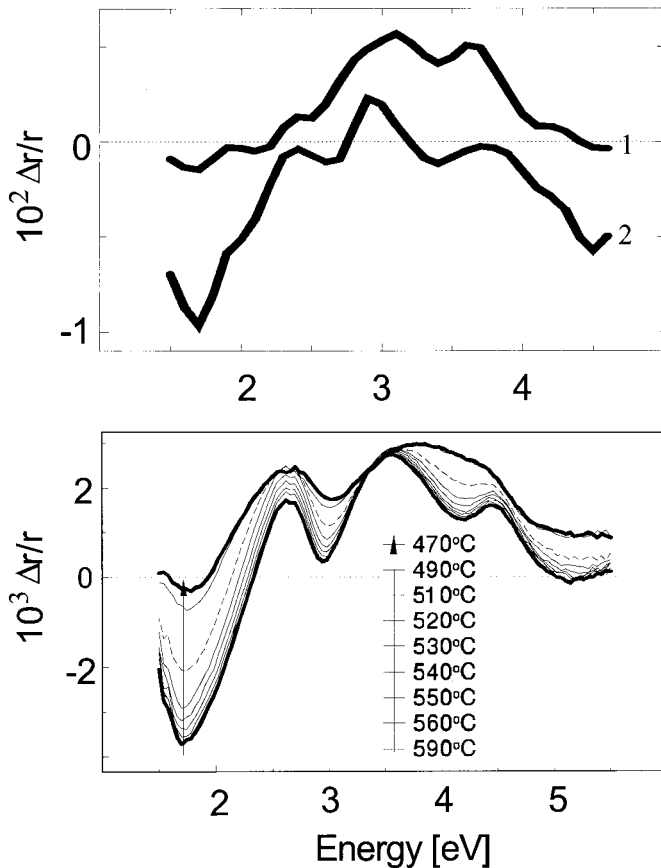


Fig. 8. Comparison of calculated (upper part) and measured (lower part, [58]) RA spectra for InP(001) 2×4 surfaces of different stoichiometries. The structures being most favourable from the energetical point of view and used in the calculations are shown in Fig. 6 ($1 \triangleq \delta$; $2 \triangleq$ mixed dimer)

tent from the mixed-dimer to the $\beta 2$ structure a significant development of the spectra is obvious. Whereas a pronounced negative anisotropy occurs for the most In-rich preparation conditions (mixed-dimer) with a strong minimum somewhat below the photon energy of about 2 eV, a broad positive RA feature between 2 and 4.5 eV develops with the reduction of the number of In–In surface bonds. The principal development of the RA lineshape and its correlation with the surface stoichiometry seems to be in agreement with the experimental findings [15, 58].

More in detail, the influence of such a development from a less In-rich to a more In-rich surface is demonstrated in Fig. 8 by heating the InP(001) surface under conservation of the 2×4 translational symmetry [58]. The agreement is reasonable. It seems that the experimental spectrum develops from that related to the δ -reconstruction to the lineshape being characteristic for the mixed-dimer model. The most important feature in the RA spectrum of the latter reconstruction is the negative anisotropy around 1.7 eV. It is correlated with the bonds and dangling bonds of the surface In atoms. From the six σ -like In–In surface bonds mainly the two bonds between the topmost In

atom and a neighbouring In atom in the nominal surface layer contribute to the occupied initial states of the corresponding optical transitions. The final states are mostly related to empty dangling bond states at surface In atoms [14]. The relative broad positive anisotropy between 2.5 and 4 eV is a consequence of optical transitions between states related to the two P–P dimers (cf. Fig. 6) and surface resonances. The initial dimer states are governed by the π -bonds, whereas various states (including bulk-like ones) contribute to the final states. All spectra exhibit a derivative-like feature around 2.5 eV, caused by transitions between surface-modified bulk states. Its energetical position coincides with the calculated position of the E_1 peak.

4. Summary

In conclusion, we have demonstrated part of the progress recently made in the theoretical description of surface optical properties, focusing on the reflectance anisotropy. The theory is now able to predict surface optical spectra with a precision that allows the identification of a certain surface structure. This was possible because of improvements concerning the numerical treatment of the spectra, the better inclusion of many-body effects to really account for the excitation aspect, and the *ab initio* derivation of surface phase diagrams. The polar InP and GaP(001) 2×4 surfaces have been considered as model surfaces in this respect.

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