

Layer-by-layer analysis of surface reflectance anisotropy in semiconductors

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We propose a method to obtain the layer-resolved contributions to the reflectance anisotropy signal of semiconductor surfaces which are modeled using the slab approach. Following this method, a microscopic formulation based on the semiempirical tight-binding approach is used to calculate the reflectance anisotropy of two InP(001) surface structures possibly relevant to standard gas-phase epitaxy conditions. It is shown that (i) the elimination of the anisotropy signal from the bottom layers of the slab is essential to correctly compare with the experiment and (ii) the strong low-energy anisotropy characteristic for gas-phase-grown InP surfaces arises from the uppermost atomic layers.

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Linear optical spectroscopic probes have been employed to investigate very different physical aspects of surfaces with great success.¹ In particular, reflectance anisotropy spectroscopy (RAS) measures the difference between the normal-incidence optical reflectance of light polarized along the two principal axes in the surface plane as a function of the photon energy. Since the bulk optical properties of cubic crystals are isotropic, any observed anisotropy must be related to the lower symmetry of the surface. RAS data are typically obtained in the visible-ultraviolet spectral range,² thus providing information about electronic structure modifications due to the creation of the surface, reconstructions, adsorbates, surface electric fields, etc.^{3,4} The theoretical approaches used to model RAS spectra range from phenomenological models,⁵ bond polarizable models,^{6,7} and semiempirical models,⁸ to *ab initio* calculations^{9–11} in combination with Green's-function methods which allow for the inclusion of electron-hole attraction effects.¹² Despite these efforts, the actual physical origin of the surface-related optical anisotropies remains an open question. The discussion was fueled by the finding that RAS data on chemically saturated surfaces often resemble the energy derivative of the corresponding bulk dielectric function $\epsilon_B(\omega)$, whereas ϵ_B -like spectra may occur for surfaces with unsaturated dangling bonds.¹³ The suggestions to explain these findings range from photon-induced localization of the electron wave packets,¹⁴ the surface termination effect,¹⁵ the influence of the surface electric field,¹⁶ and strain-induced dichroism at the bulk critical points of the dielectric function on the surface optical response.¹⁷

A qualitative and quantitative understanding of the possibly different origins of surface-induced optical anisotropies is obviously an essential requirement for the full exploitation of the physical and chemical information contained in RAS spectra. Therefore, in the present paper a method is proposed to allow us to analyze the spatial origin of the RAS signal with atomic layer resolution. As an example two surface structures that have been proposed to occur during the gas-phase growth of InP(001) are investigated.

To model the semi-infinite crystal we use a slab consisting of N atomic layers, extending from $z=0$ to $z=Nd$, d being the interlayer distance. We define the RAS signal as

$$\mathcal{R} \equiv \Delta R_x / R - \Delta R_y / R, \quad (1)$$

where ΔR_i is the surface-related change in the reflectivity and R is the usual Fresnel reflectivity, with $i=x$ or y . The surface contribution at normal incidence is given by¹⁸

$$\Delta R_i / R = 4(\omega/c) \text{Im}[4\pi D \alpha_{ii}(\omega) / (\epsilon_B(\omega) - 1)], \quad (2)$$

with $\hbar\omega$ being the incident photon energy, c the speed of light, and D half of the slab thickness. The imaginary part of the half-slab polarizability, α_{ij} , is related to the transition probability induced by the radiation between slab eigenstates,¹⁸

$$\text{Im}[4\pi D \alpha_{ij}(\omega)] = \gamma(\omega) \sum_{v,c,\vec{k}} P_{v,c}^i(\vec{k}) P_{c,v}^j(\vec{k}) \Delta_{v,c}(\vec{k}, \omega), \quad (3)$$

where $\vec{P}_{m,n}$ is the matrix element of the momentum operator, $\vec{P} = -i\hbar\vec{\nabla}$, between m and n , with $m, n = v$ valence-initial or c conduction-final states at point $\vec{k}$ in the two-dimensional Brillouin zone. Also, $\gamma(\omega) = 4\pi^2 e^2 / m^2 \omega^2 A$, with A the sample area, and $\Delta_{v,c}(\vec{k}, \omega) = \delta[E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega]$, where the Dirac's delta takes care of energy conservation, with $E_n(\vec{k})$ the slab eigenvalues. In Eq. (3), the i -Cartesian component of $\vec{P}_{m,n}$ is related to the operator associated with the expectation value of the polarization, whereas its j -Cartesian component comes from the operator associated with the perturbation induced by the electromagnetic field. In other words, the induced dipole moment, $\vec{p}$, is related to the perturbing electric field, $\vec{\mathcal{E}}$, by the well-known relation $p_i = \alpha_{ij} \mathcal{E}_j$.

The slab used in the calculation has a front and a back surface. For nonpolar faces of binary semiconductors, such as the (110), it is always possible to have the front and the back surfaces identical, but for polar faces, such as the (001),

this is not the case and the back surface is different from the front surface. Then, the question as to how one should obtain $\mathcal{R}$ of either the front or the back surface arises. To this end, one has to introduce a *cut* function associated with the quantum-mechanical operator that gives the induced polarization in Eq. (3). Thus, we write the matrix elements of the modified momentum operator as

$$P_{v,c}^i \rightarrow \mathcal{P}_{v,c}^i = \frac{1}{2} \sum_{\ell} [P_{v,\ell}^i(S(z))_{\ell,c} + (S(z))_{v,\ell} P_{\ell,c}^i], \quad (4)$$

where $[S(z)]_{m,n}$ are the matrix elements of the cut function, $S(z)$, and we have introduced a complete set of eigenstates denoted by ℓ that runs over all v and c states. The typical choice for $S(z)$ is a step function that is 1 for one-half of the slab and zero for the other, depending on whether one wants to compute $\mathcal{R}$ for the front or the back surface. However, this function can be generalized in such a way that one can isolate the contribution of every atomic layer to α_{ij} , and thus one can study the optical anisotropy of every single layer. Indeed, taking z_n as the z position of the n th layer we can write

$$S(z) = \Theta(z - z_n + d/2) \Theta(z_n + d/2 - z) \equiv S(z_n), \quad (5)$$

so from Eqs. (3) and (4) we obtain the n th atomic layer polarizability as

$$\text{Im}[4\pi D \alpha_{ij}(n)] = \gamma(\omega) \sum_{v,c,\vec{k}} \mathcal{P}_{v,c}^i(n, \vec{k}) P_{c,v}^j(\vec{k}) \Delta_{v,c}(\vec{k}, \omega), \quad (6)$$

with

$$\mathcal{P}_{v,c}^i(n, \vec{k}) = \frac{1}{2} \sum_{\ell} [P_{v,\ell}^i(\vec{k})(S(z_n))_{\ell,c} + (S(z_n))_{v,\ell} P_{\ell,c}^i(\vec{k})]. \quad (7)$$

Then,

$$\alpha_{ij}^{\lambda} = \sum_{n_i}^{n_f} \alpha_{ij}(n) \quad (8)$$

gives the contribution of the front (back), $\lambda = f(b)$, surface for $n_i = 1$ and $n_f = N/2$ ($n_i = N/2 + 1$ and $n_f = N$), where $\alpha_{ij}^f + \alpha_{ij}^b = \alpha_{ij}$. Since Eq. (2) is linear in α_{ii} , so is Eq. (1), and then besides using Eq. (8) to obtain $\mathcal{R}$ of the front and back surfaces, we can use $\alpha_{ii}(n)$ to obtain $\mathcal{R}$ for each atomic layer of the slab. If the electronic wave functions are expanded into (or projected onto) atomic orbitals, then $(S(z))_{\ell,m} = S(z_n) \delta_{\ell,m}$ where $S(z_n) = 1$ if the position z_n corresponds to the atom described by the quantum label $\ell = m$, and is zero otherwise.

In the following we use the semiempirical tight-binding (SETB) formalism with a sp^3s^* basis to describe the slab electronic structure, which allows for a fast while still physically sound interpretation of RAS spectra,⁸ and is particular suitable in the present context, because it allows for a natural assignment of the electronic states to specific atomic layers. Our approach of separating the atomic layer contributions to

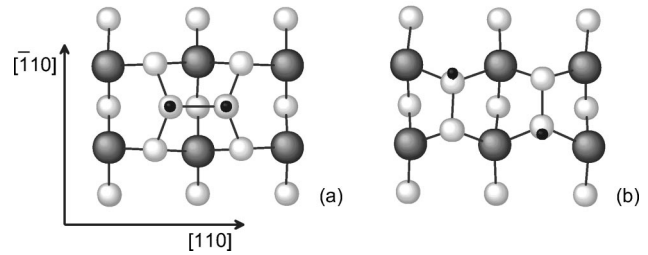


FIG. 1. Top view of (a) 1D and (b) 2D InP(100):H surface structures. Dark (light, small) symbols indicate In (P, H) atoms.

$\mathcal{R}$ is not restricted to a tight-binding description, but may also be combined with plane-wave or finite-difference schemes.¹⁹

Because optical spectroscopies do not require ultrahigh-vacuum conditions, they are increasingly being used to monitor gas-phase epitaxy processes. Recently the (001) surface structures occurring during the gas-phase growth of InP have been investigated,²⁰ where two of them stand out as energetically most favorable. One consists of single, H-passivated P dimers on top of a P-terminated substrate, and it may occur for P- and H-rich surface preparation conditions (labeled 1D in Fig. 1). If the surface is less P rich, periodic chains of oppositely buckled P dimers on top of an In-terminated substrate, with one H atom bonded to the down atom of the P dimer, may form (labeled 2D in Fig. 1). The bottom of the slab is P terminated and saturated with H. Since the SETB parameters for P-P interaction are not known, we started from the InP parameters of Ref. 21 and adjusted the parameters that describe the nearest-neighbor overlap integrals in such a way that $\mathcal{R}$ of the 2D reconstruction coincides the best with the experimental signal.²² The values found are $V_{ss\sigma} = -1.34$ eV, $V_{sp\sigma} = 0.73$ eV, $V_{pp\sigma} = 0.26$ eV, $V_{pp\pi} = -0.18$ eV, and $V_{s^*p\sigma} = 1.36$ eV.

In Fig. 2 we show $\mathcal{R}$ for each layer of the 2D reconstruction.

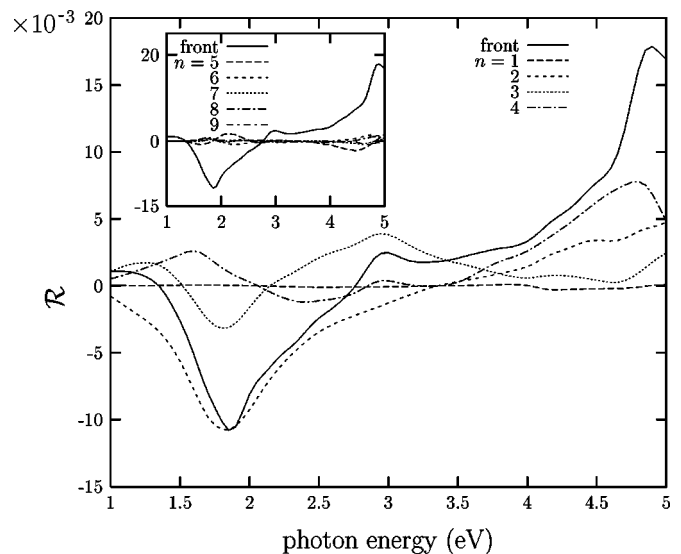


FIG. 2. RAS spectra for the 2D surface structure. The solid line is the total contribution from the front surface, and the other lines are the contributions from each atomic layer.

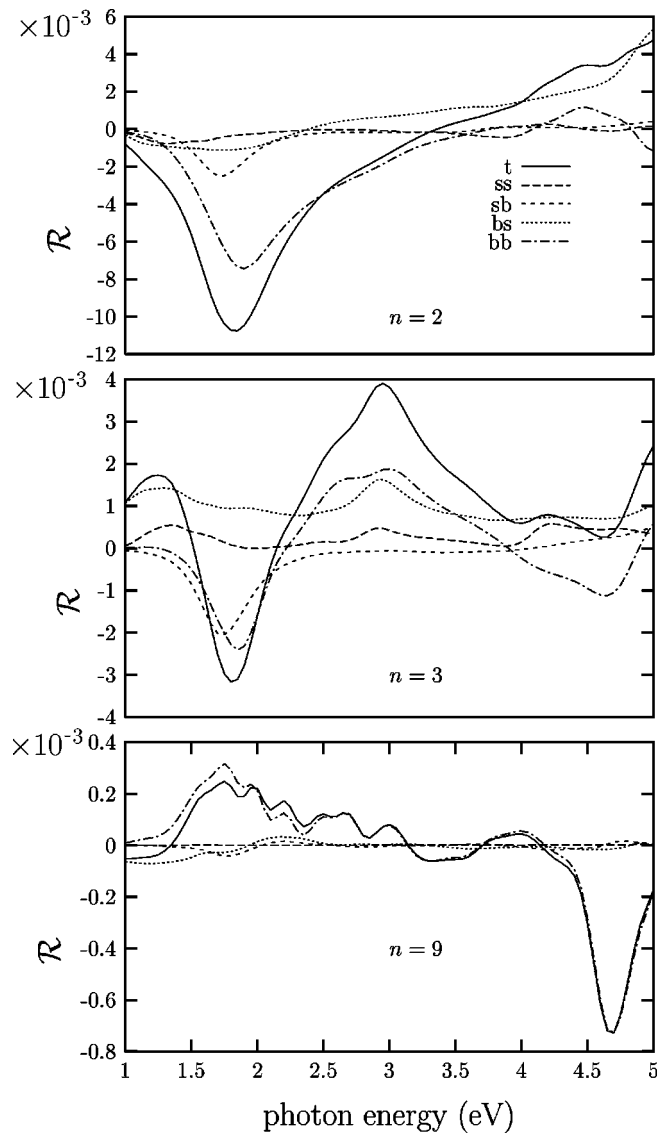


FIG. 3. RAS spectra for the 2D surface structure. The *ss*, *sb*, *bs*, and *bb* valence to conduction electronic band transitions are shown for the second ($n=2$), third ($n=3$), and ninth ($n=9$) layers. The solid line is the total contribution for each layer as shown in Fig. 2. Note the smaller vertical scale in the lower panel.

tion along with the front surface $\mathcal{R}$ obtained through Eq. (8). We see that for $n=1$ (H partially saturating the P dangling bonds), the signal is almost null, and the main contribution to the front surface signal comes from the P dimers ($n=2$), and from $n=3$ and 4, which correspond to the next In and P layers, respectively. Below the fifth layer (In), $\mathcal{R}$ is small, and as we approach the bulk of the material $\mathcal{R}$ is basically zero, as it must be from symmetry considerations. These results are similar to those of Ref. 7 for the Si(100)2 $\times$ 1-As surface, obtained through the discrete dipole model. We also see that the feature at 1.8 eV has its main contribution from layers two and three, whereas the feature at 3.0 eV comes from layers three and four, which agrees with the common idea that features below the energy gap are surface related, whereas features above the energy gap are bulk related.

To further analyze this fact, we present in Fig. 3 $\mathcal{R}$ for

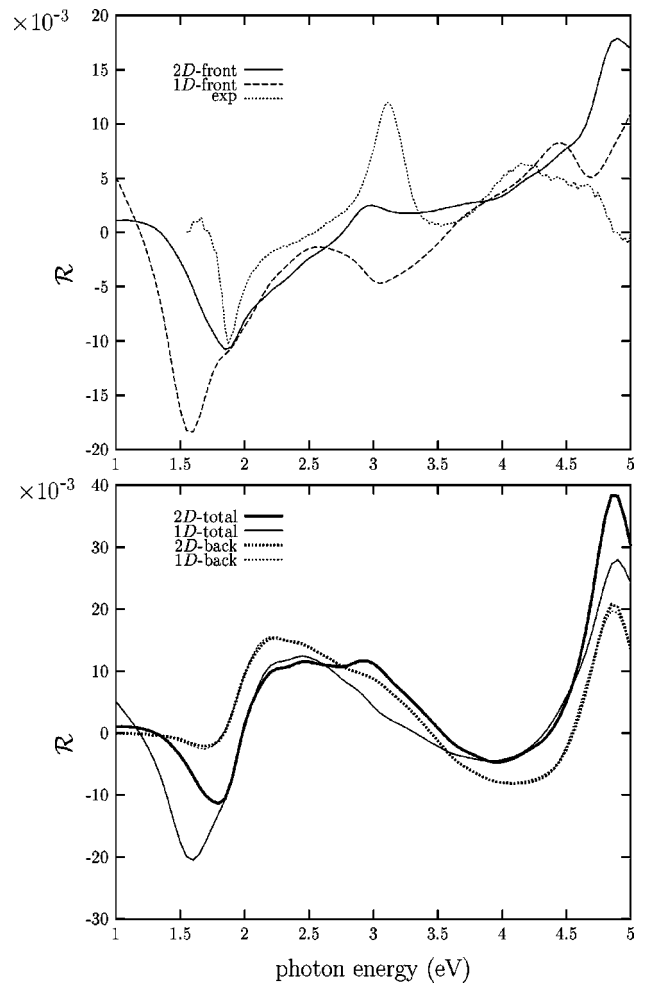


FIG. 4. Top panel: Front RAS spectra for the 1D and 2D surfaces along with the experimental results of Ref. 24 (dotted line). Lower panel: total (solid lines) and back-surface (dotted lines) RAS signals for the same reconstructions of the top panel.

layers two, three, and nine, where we have decomposed the spectra into its contributions from valence- to conduction-electronic transitions, where each electronic state is classified according to its surface (*s*) or bulk (*b*) wave-function character.²³ For layer two (P dimers), we see that the main contribution to the 1.8-eV feature comes from *sb* and *bb*. For the third layer the same feature has contributions mainly from *sb*, and for the 3-eV feature the contributions come from *bs* and *bb*. Finally, the ninth layer $\mathcal{R}$, besides being an order-of-magnitude smaller than the one from the previous two cases, is only dominated by the *bb* contribution. From this figure we learn that a bulk layer is dominated by *bb* transitions, as should be expected, but as we move toward the surface and the symmetry becomes broken, it is the interplay of the surface states and the *surface-modified* bulk states that gives rise to the RAS signal. One would expect naively that only the *surface-related* RAS features, i.e., those below the gap energy, should be dominated by *s*-related transitions, but the *surface-modified b* states give also important contributions.

In Fig. 4 we compare $\mathcal{R}$ from the front surface of the 1D and the 2D reconstructions along with the experimental re-

sults of Ref. 24. We note that $\mathcal{R}$ of 1D is in disagreement with the experimental trace: the 1.9-eV experimental negative feature is at 1.6 eV and more importantly, the 3.1-eV experimental positive feature is a negative dip at 3.0 eV. On the other hand, the overall agreement of the 2D is better, where we note a small 0.1-eV redshift of the theoretical spectrum, and a smaller intensity for the 3.1-eV feature. Above 3.5 eV, the agreement is good for both surfaces, although the feature at 4.9 eV is not seen in the experiment, since perhaps it is out of the measured range. Our results in favor of the 2D structure are also confirmed by scanning tunneling microscopy,²⁵ and the theoretical results of Ref. 20. We also show the total and back surface $\mathcal{R}$'s. The former is different for both surfaces and from the experiment, and the latter is also different from the experimental signal, but almost identical for both reconstructions, since the back surface is the same in either case. Thus, it is clear that the H-terminated bottom layer of the slab gives rise to an artificial RAS signal which needs to be eliminated for a meaningful comparison with experiment.

We have presented a method to calculate the contributions of individual surface layers to the reflectance anisotropy. Using the computationally less demanding SETB method, we obtained that the InP(001) surface that shows oppositely buckled and partially H-terminated P dimers has a RAS signal in good qualitative agreement with the experimental result for gas-phase epitaxy-grown samples. The analysis through the layer-by-layer decomposition of the RAS signal shows the surface-specific RAS origin and the interplay of the surface- and bulk-surface-modified electronic states. This scheme sheds new light on the physical process of this useful spectroscopic optical probe.

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²²We also tried to adjust the parameters for the 1D reconstruction and did not get good agreement with the experiment, indicating that 1D may not be observed experimentally.

²³If the sum of the modulus square of the wave function for the first N_s layers is larger than the equivalent sum of the bulk layers [i.e., from $n=N_s+1$ up to $n=N-(N_s+1)$], the state is an *s* state, otherwise a *b* state (in our case $N=19$ and $N_s=5$).

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