

Surface versus crystal-termination effects in the optical properties of surfaces

Rodolfo Del Sole and Giovanni Onida

*Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica dell' Università di Roma Tor Vergata,
Via della Ricerca Scientifica, I-00133 Roma, Italy*

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We prove, by realistic microscopic calculations within the sp^3s^* tight-binding method for GaAs(110) and GaAs(100), that the surface optical properties are not influenced by long-range crystal termination effects, and hence that they can be consistently studied considering slabs of limited thickness (20–30 Å). The origin of derivativelike and bulklike line shapes in reflection anisotropy spectra is also discussed, analyzing the effects arising from possible surface-induced reduction, broadening, and shifting of the bulk spectrum near the surface. [S0163-1829(99)01123-6]

I. INTRODUCTION

Reflectance anisotropy spectroscopy (RAS) and surface differential reflectance (SDR) are surface-sensitive optical techniques, and are used to obtain information on the atomic and electronic structures of surfaces.¹ In the early times of these spectroscopies, the spectra were explained in terms of transitions across surface states, although this view has been contrasted by calculations, showing that surface-geometry effects could also determine the spectra through surface perturbations on the optical matrix elements of transitions across bulk states.² Now the attitude seems to be reversed: after realizing that many RA line shapes are similar to the imaginary part of the bulk dielectric function, or to its energy derivative, it is a growing belief that surface optical spectra are mostly determined by bulk effects, and therefore, not very useful as a tool of surface characterization. In this paper, we discuss the origin of these bulklike features, and at the same time emphasize the presence in optical spectra of other features, more related to the surface structure.

In 1996, Rossow, Mantese, and Aspnes³ recognized that RAS data on chemically saturated surfaces generally resemble the energy derivative line shapes of the corresponding bulk spectra, $d \text{Im}[\epsilon_b(\omega)]/d(\omega)$, while surfaces with unsaturated dangling bonds (DB's) often yield RAS line shapes resembling the bulk spectrum, $\text{Im}[\epsilon_b(\omega)]$. They explained the latter line shapes in terms of surface-induced changes of the electron-hole interaction and of local fields, while derivativelike spectra were explained in terms of surface perturbations on the energies of bulk states. From these findings, they inferred the occurrence of shorter lifetimes of electrons and holes near the surfaces. We show here that this deduction is not necessary. Furthermore, we demonstrate the existence of other mechanisms able to produce energy-derivative line shapes.

A further step along the way of attributing most RAS and SDR features to bulk effects has been done by Uwai and Kobayashi (UK) in 1997.⁴ They measured surface photoabsorption (SPA) spectra for different conditions of the GaAs(001) and GaAs(111) surfaces, from which the changes of the surface dielectric tensor were extracted. The imaginary parts of such changes have peaks at 2.6–3 eV and at 4.5–4.7 eV, close to the main structures, E_1 and E_2 , of the bulk dielectric function. The line shapes are similar to the imaginary part of the bulk dielectric function in the case of the

(001) surface, and to its derivative for the (111) surface. UK conclude that these two peaks are not due to transitions involving surface states, but to modified bulk electronic transitions. They claim that the surface termination effect, first discussed by one of the present authors in 1975,⁵ is responsible for the occurrence of bulklike features in surface spectra. According to UK, this effect mostly consists in a reduction of the polarizability below the surface, arising from the quenching of bulk-state wave functions near the surface, due to their vanishing outside the crystal. This might be a long-range effect, extending one hundred Angstroms below the surface, which might be hardly included in slab calculations. We show here that, although the crystal-termination effect is in fact present, the way it has been described by UK is rather naive; not a bare reduction of the polarizability, but a distortion of its line shape must occur (and indeed occurs), to produce a nonvanishing RAS or SDR signal. However, the resulting effect is by no means of long range, and is in fact included in slab calculations. Moreover, while the crystal-termination effect often yields derivativelike line shapes, we have not found bulklike spectra arising from it.

The GaAs(110) surface is a good test case for our calculations and discussions, because of its well-defined atomic structure and for the occurrence of (modest) surface effects partially overlapping in energy with (predominant) bulk effects.^{6,7} The As-rich GaAs(100) $\beta 2(2 \times 4)$ surface will also be considered.

II. THEORY

We calculate the surface contribution to reflectance, that is its relative deviation with respect to Fresnel formulas, according to the three-layer model⁸

$$\frac{\Delta R_i}{R} = \frac{4\omega}{c} \cos \theta d \text{Im} \left[\frac{\epsilon_{si}(\omega) - \epsilon_b(\omega)}{\epsilon_b(\omega) - 1} \right], \quad (1)$$

for s -light polarized parallel to the i direction ($i=x$ or y) in the surface plane, where θ is the angle of incidence, d the depth of the surface layer, $\epsilon_{si}(\omega)$ is the ii diagonal component of the surface-layer dielectric tensor, and $\epsilon_b(\omega)$ is the isotropic bulk dielectric function. For p -light incident in the iz plane, the anisotropic three-layer model yields¹

$$\frac{\Delta R_i}{R} = \frac{4\omega}{c} \cos \theta d \operatorname{Im} \left\{ \frac{[\varepsilon_{si}(\omega) - \varepsilon_b(\omega)][\varepsilon_b(\omega) - \sin^2 \theta] + \varepsilon_b^2(\omega) \sin^2 \theta [1/\varepsilon_{sz}(\omega) - 1/\varepsilon_b(\omega)]}{[\varepsilon_b(\omega) - 1][\varepsilon_b(\omega) \cos^2 \theta - \sin^2 \theta]} \right\}. \quad (2)$$

The surface-layer dielectric tensor, assumed to be diagonal, is obtained by subtracting the bulk dielectric function from the calculated slab dielectric tensor, with a suitable choice of the surface-layer depth d . The reflectivity for s light comes out to be independent of the choice of d , coincident with the microscopic formulas not relying on the three-layer model. This model is instead needed to obtain p -light reflectivity by avoiding the computationally very demanding inversion of the dielectric susceptibility tensor.

III. RESULTS

We start by calculating the normal-incidence reflectance anisotropy (RA), $2(R_x - R_y)/(R_x + R_y)$, of GaAs(110). The latter is the cleavage surface of GaAs, and, despite being not reconstructed, undergoes large relaxations. Its equilibrium structure, known as the “rotation-relaxation model,” is well known both from the experimental and the theoretical sides: the surface As atoms relax toward the vacuum, and Ga atoms move in the opposite direction, recovering a quasiplanar sp^2 bonding with their three As neighbors.⁹ We represent the surface using a slab of 31 atomic layers, where the actual atomic positions are taken from a Car-Parrinello total energy minimization.¹⁰ Since the slab has two equivalent surfaces, the computed slab polarizability must be divided by two. We then also consider a polar surface of GaAs: the As-rich (100) $\beta 2(2 \times 4)$. The latter is known to be the stable reconstruction for this surface,¹¹ and is a regular array of two As dimers and two dimer vacancies (the unit cell contains only two As dimers), aligned along the $[\bar{1}10]$ direction. Also in this case, the actual atomic positions are taken from a Car-Parrinello total energy minimization.¹² In the case of GaAs(100), since geometry does not allow to build a slab with two equivalent surfaces, the calculation is done for a system with only one surface reconstructed, i.e., by including a real-space cutoff function (a squared cosine, approaching one on the interesting surface and zero on the other), in the optical transition probability calculations, to eliminate the contribution of the back surface.¹³ The electronic states of the slab, as well as of those of bulk GaAs, are calculated according to the sp^3s^* tight-binding method, as in Ref. 2. The As-As tight-binding interaction parameters are those of Ref. 14. The imaginary part of the slab dielectric function is obtained by considering transitions at a number of k points in the irreducible part of the two-dimensional Brillouin Zone (IBZ). The first issue we address is the number of k points that are needed to obtain a good convergence. In Fig. 1, we show the RA of GaAs(110) calculated with 256, 1024, and 4096 special k points in the IBZ; the curves corresponding to the first two cases are clearly distinct from each other. The calculation with 4096 k points, instead, is almost coincident with that with 1024 k points. This means that 1024 k points are needed to achieve full quantitative convergence of the GaAs(110) RA. This result might be a peculiar property of this and similar surfaces. In the case of the GaAs(100)

$\beta 2(2 \times 4)$ surface, a good convergence of the spectrum is already obtained using a number of k points equivalent to 64 in the (1×1) surface cell. Similar calculations carried out on Si(110):H show that the RA spectrum is already converged with 64 k points (usually, calculations are made with 64 k points or less,^{2,6,7} since, even with a well-converged k -point summation, only qualitative accuracy can be achieved, due to the neglect of excitonic and local-field effects).

The calculated RAS for GaAs(110) is qualitatively similar to previous calculations, carried out using tight-binding or *ab initio* methods, and to experiments.^{6,7,15} The peak at about 2.9 eV embodies a substantial contribution of transitions across surface states or resonances (at variance with Ref. 6, but in agreement with Refs. 7 and 15), while the higher-energy structures are essentially due to transitions across surface-perturbed bulk states. The main effect of the k -point convergence achieved in the present calculation was to reduce the intensity of the dip just above the 2.9 eV peak and of the subsequent structures.

Having achieved quantitative convergence with respect to the number of k points, we can look now at the convergence with respect to the number of layers, which is the main interest here, since changes in line shapes occurring for very thick slabs would indicate the presence of the long-range effect assumed by UK.⁴ In Fig. 2(a) we show the GaAs(110) RA calculated using slabs of 11, 31, and 93 layers and 1024 k points. The latter two curves are almost indistinguishable, while the 11-layer curve is also close to them. This means that the calculation has already converged with 31 layers, and that the aforementioned long-range effect does not occur. The same is true for the polar (100) surface: in Fig. 2(c), we show the calculated RA for the GaAs(100) $\beta 2(2 \times 4)$

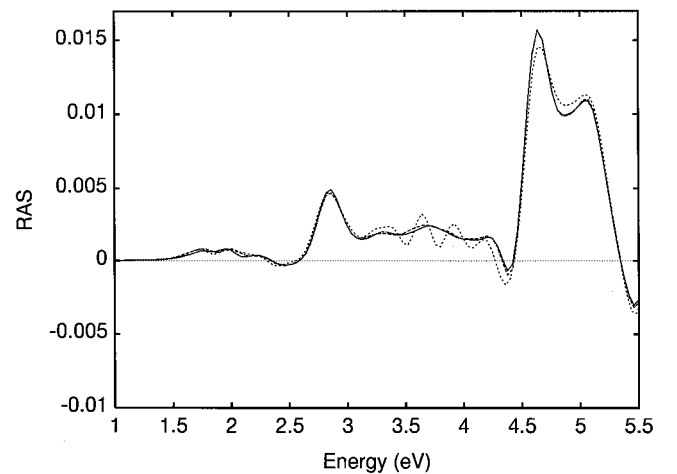


FIG. 1. Calculated reflection anisotropy spectrum of the GaAs(110) surface, and its convergence with respect to the Brillouin-zone sampling. Full line: 4096 k points in the irreducible wedge of the surface Brillouin zone; long-dashed line: 1024 k points; dotted line: 256 k points. In the latter case, full convergence has not yet been reached.

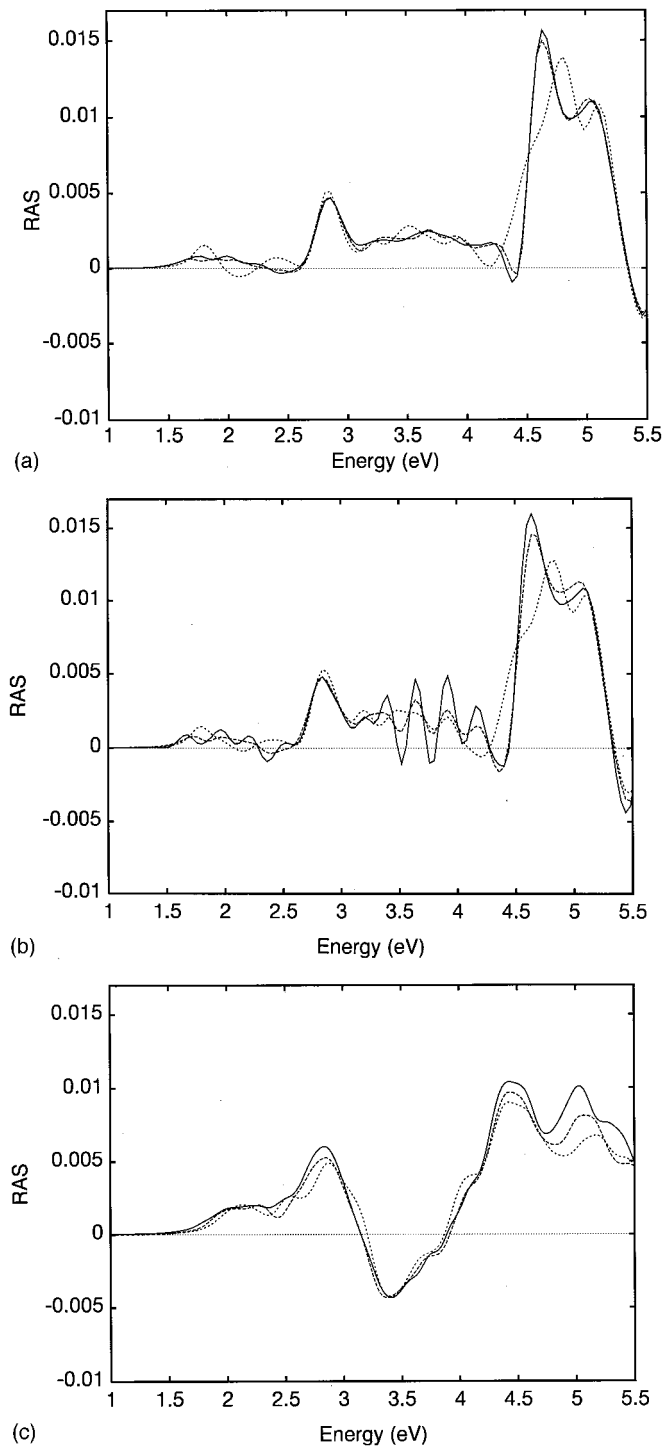


FIG. 2. (a) Convergence of the theoretical RA spectrum of GaAs(110), calculated using 1024 k points, with respect to the thickness of the slab (number of atomic layers) used in the calculation. Full line: 93 layers; dashed line: 31 layers; dotted line: 11 layers. The results for 31 and 91 layers are almost identical. (b) The same, calculated using 256 k points. (c) Convergence of the theoretical RA spectrum of GaAs(100) $\beta 2(2 \times 4)$, calculated using 8 k points [equivalent to 64 in the (1×1) surface cell], with respect to the thickness of the slab. Full line: 40 layers; dashed line: 20 layers; dotted line: 16 layers.

surface, where small differences show up using slabs of 16, 20, and 40 layers. The slow convergence with slab thickness observed in calculations⁷ when a smaller set of k points is

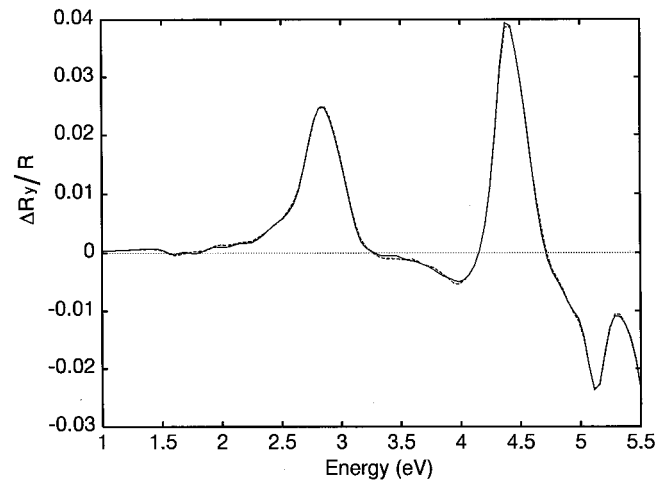


FIG. 3. Surface contribution to reflectance for p -light incident in the y - z plane at 60° , for GaAs(110) slabs of 31 layers (dashed line) and 91 layers (full line), using 1024 k points in the SBZ. The y direction is parallel to the chains in the surface plane, while z is perpendicular to the surface.

used is therefore due to the error caused by the small number of k points, which randomly varies with the number of planes. This is nicely demonstrated by Fig. 2(b), where the same series of slabs as in Fig. 2(a) (11–31–93 layers) has been used to compute the GaAs(110) RAS spectrum with a set of 256 k points.

In view of the different structures of Eq. (1), for s light, and Eq. (2), for p light, one could speculate that the long-range effect might cancel in the former case, and appear in the latter. To check this possibility, we present in Fig. 3 the surface contribution to p -light reflectance calculated using the anisotropic three-layer model at an angle of incidence of 60° . Again no difference is present between the curves calculated with 31 and 93 layers, definitely showing that surface optical properties are well converged with slabs of 31 layers. The present results increase our confidence in slab calculation, not only since very long-range effects, which can be hardly embodied therein, are excluded, but also because thin slabs, as the 11- and 16-layer ones, which are the only ones that can be afforded in *ab initio* calculations,⁷ already yield rather good results.

Let us discuss now in more detail the crystal-termination effect invoked by UK.⁴ It has been first addressed by one of the present authors in connection with the reflectivity at the direct minimum gap of a semiconductor.⁵ By disregarding the microscopic structure of the surface, and describing it just as an infinite potential barrier preventing electrons from escaping into vacuum (the crystal termination), the reflectivity was obtained starting from the wave functions calculated according to the effective-mass approximation. Since the wave functions must vanish at the crystal-termination plane, the envelope plane waves occurring in an infinite crystal are replaced by sinetype standing waves. When looking at the imaginary part of the local dielectric function, $\text{Im}[\varepsilon(z, \omega)]$, this yields a region below the surface where this quantity is smaller than in the bulk crystal. The depth of such a region is of the order of π/k_z , k_z being the largest wave vector of the relevant transitions. In the case of the minimum gap, hence, $k_z = [2m^*(\hbar\omega - E_g)/\hbar^2]^{1/2}$, where m^* is the reduced

electron-hole effective mass and E_g the direct gap energy. By taking an effective mass of 0.1 and $\hbar\omega - E_g$ as 0.1 eV, we estimate this depth to be of the order of 60 Å. This is the quenching of the (bulk) dielectric function below the surface, that UK assume as the most important effect. However, crystal termination affects the optical properties also in another way: since the matrix elements of the momentum operator must be calculated between the surface-perturbed wave functions (sine-type in the case discussed here), they are different from those of the infinite crystal. More explicitly, k_z is no longer conserved in subsurface optical transitions; the breaking of this selection rule yields spectra distorted with respect to (namely, broader than) the corresponding bulk spectra, acting as an additional broadening localized near the surface. We will show below that this additional broadening is the most important crystal-termination effect influencing the surface optical properties of GaAs.

Differently from the case discussed above, the main structures of bulk spectra, which yield the most prominent bulk-related structures in RAS and SDR, are due to transitions at saddle points of the joint density of states. The characteristic k_z at saddle points is much larger than at the direct gap, because a large region of Brillouin Zone is available for optical transitions at the saddle-point energy. For instance, vertical transitions along all the Λ line are responsible for the E_1 structure in GaAs. Hence, the largest k_z is of the order of the BZ boundary, π/a , and the depth of the surface-perturbed region is of the order of the lattice constant a . This explains why we have not found in Figs. 2 and 3 any indication of long-range effects close to saddle-point energies.

The simplest model of quenching is to assume that the polarizability is completely suppressed within some depth d below the surface. This, however, would be equivalent to shift the surface by d , and would not give any contribution to the reflectance. Hence we consider a slightly different model, where the polarizability is partly quenched, say 50%, in a depth d . In practice we assume, within the depth d , a surface dielectric function of the form

$$\varepsilon_{si}(\omega) = f_i \cdot \varepsilon_b(\omega - \Delta\omega_i, \gamma_i) \quad (3)$$

where $\varepsilon_b(\omega)$ is the bulk dielectric function, f_i (≤ 1) represents the quenching, γ_i is the broadening (possibly different from the bulk one), and $\Delta\omega_i$ is a possible frequency shift. When $\Delta\omega_i = 0$, $\gamma_i = \gamma_{bulk}$, and $f_i = 1$, $\varepsilon_{si}(\omega)$ coincides with the bulk dielectric function. Taking $f_i < 1$ with $\gamma_i = \gamma_{bulk}$ and $\Delta\omega_i = 0$ would not modify the s -light reflectivity, since the numerator and denominator in Eq. (1) are proportional to each other, and hence, the fraction is a real number, with vanishing imaginary part. However, this is not the case for p -light reflectivity, which may undergo some change. The full line in Fig. 4(a) shows the surface contribution calculated in this way. It is clear from the figure that this model has no relation with the output of the slab calculation (dashed line); hence, the pure quenching effect cannot account for the surface contribution to reflectance.

We consider next the pure broadening model, i.e., $f_i = 1$, $\Delta\omega_i = 0$, and $\gamma_i > \gamma_{bulk}$. Now the surface is assumed to have the same dielectric function as the bulk has, but with broader line shapes, as a consequence of the breaking of the k_z conservation near the surface. In Fig. 4(b) we show the

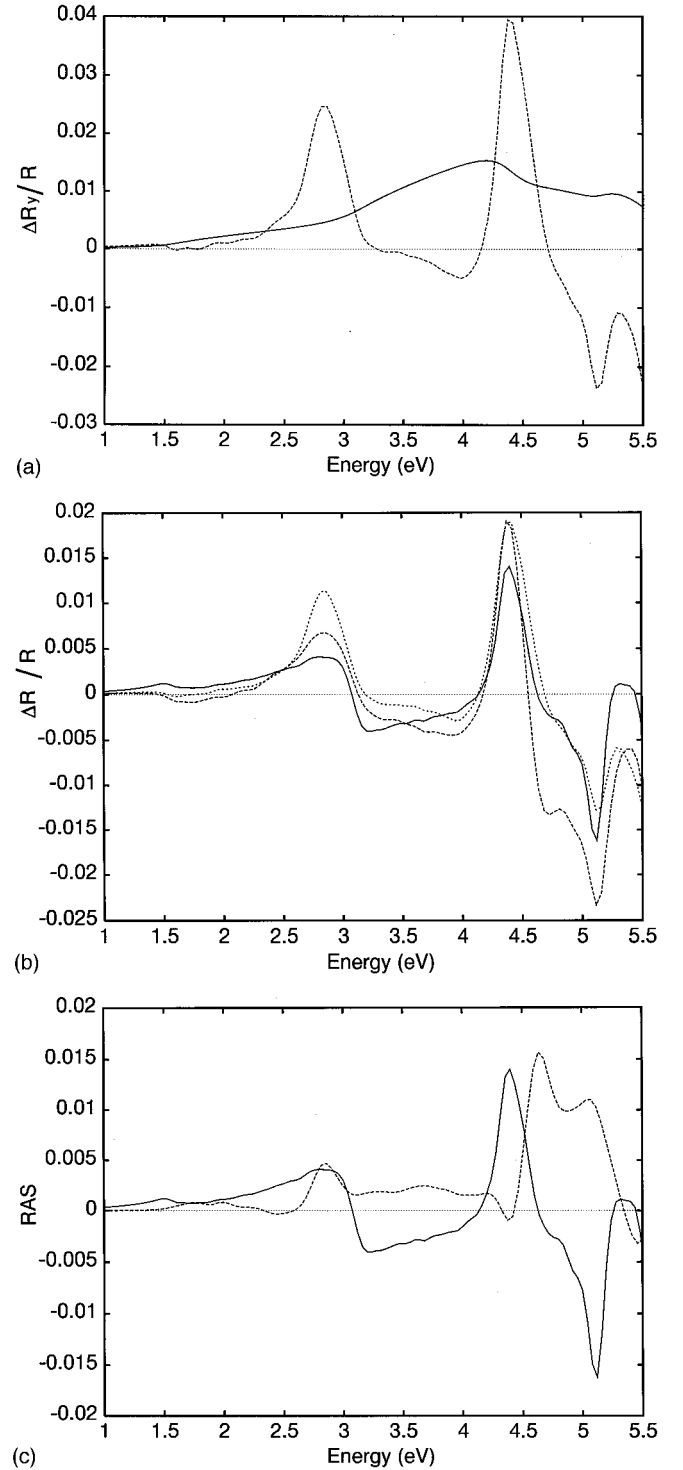


FIG. 4. (a) Microscopic calculation (110 slab) of the surface contribution to reflectance for p -light incident in the y - z plane at 60° (dashed line), compared with the results of the “quenching model” (full line); (b) Microscopic (slab) calculation of the surface contribution to reflectance for normally incident light polarized along the (110) chains (dotted line), and perpendicularly to them (dashed line), computed with a 31-layers GaAs(110) slab and 1024 k points in the SBZ, in comparison with the results of the “broadening model” (full line); (c) “Broadening model” results for the RA spectrum of GaAs (full line), compared with the microscopic calculation of Fig. 1 (dashed line).

surface contribution to the reflectivity of normally incident light, with polarization perpendicular and parallel to the $[1\bar{1}0]$ chains, as calculated from the slab polarizability (dashed and dotted lines), and according to the broadening model (full line). We assume a broadening of 100 meV at the surface, while it is 30 meV in the bulk. The curves are rather similar, showing line shapes resembling the energy derivative of the imaginary part of the dielectric function. Also the surface-state-related peak at about 2.9 eV is embodied in the broadening-model spectrum (this occurs only because the peak mentioned above overlaps in energy with the E_1 bulk structure around 3 eV). However, the differences between the broadening model and microscopic calculations, which seem to be small in this spectrum, become very large in the RA spectrum, shown in Fig. 4(c). Here, the dashed line is obtained as in Fig. 1, that is from the 31-layer slab calculation. We can produce a RA-curve according to the broadening model by assuming that the depth where the dielectric function is broader than in bulk is different for the two polarizations, or, in an equivalent manner, that also some quenching of the dielectric function occurs ($f_i < 1$), whose amount depends on the direction of light polarization ($f_x \neq f_y$). By assuming a suitable depth or quenching difference, we produce the full line in Fig. 4(c), which is of course proportional to the continuous line in Fig. 4(b). The two curves in Fig. 4(c) are markedly different, although the peak at 2.9 eV (the only spectral feature related to transitions across surface states) is present in both curves.

Hence, we can conclude by recognizing the occurrence of bulk-derivative-like features in surface optical spectra calculated for a given polarization of light, due to the broader line shape of the dielectric function near the surface. This broader line shape is due to the breaking of the k_z -conservation rule (namely, it is a crystal-termination effect), is included in slab calculations, and does not imply a shorter lifetime of electrons near the surface than in bulk. When anisotropy difference spectra are taken for GaAs(110), however, these features largely cancel, so that the surviving RA has about no relation to the broadening model. Of course, such cancelation may be smaller at other surfaces, so that derivativelike line shapes may be present in RAS and SDR spectra.

As a last point, we can assume that the (bulk) dielectric function near the surface can undergo small shifts of peak positions ($\Delta\omega_i \neq 0$), in addition to broadening and quenching. To this aim it is not needed, as assumed in Ref. 3, that electrons and holes excited in optical transitions are kept close to the surface by their short lifetimes, in order to be shifted in energy by the surface potential. The required small shifts of the peaks of the surface dielectric function may be produced by the surface perturbation on the wave functions and, consequently, on the local polarizability. It is a matter of fact that the layer-projected density of states may be different from the bulk one. The same, of course, can occur for the z -dependent dielectric function,¹⁶ whose average over the first few layers yields the surface dielectric function.

We have tried to obtain bulklike difference (RAS or SDR) spectra by suitably varying f_i , γ_i , and $\Delta\omega_i$, i.e., by shifting, broadening and quenching the bulk spectrum. By varying the parameters above, we often obtained derivativelike spectra, never obtained bulklike spectra, and sometimes hybrid spectra [see Fig. 5(a), full line]. It is worth to notice that this

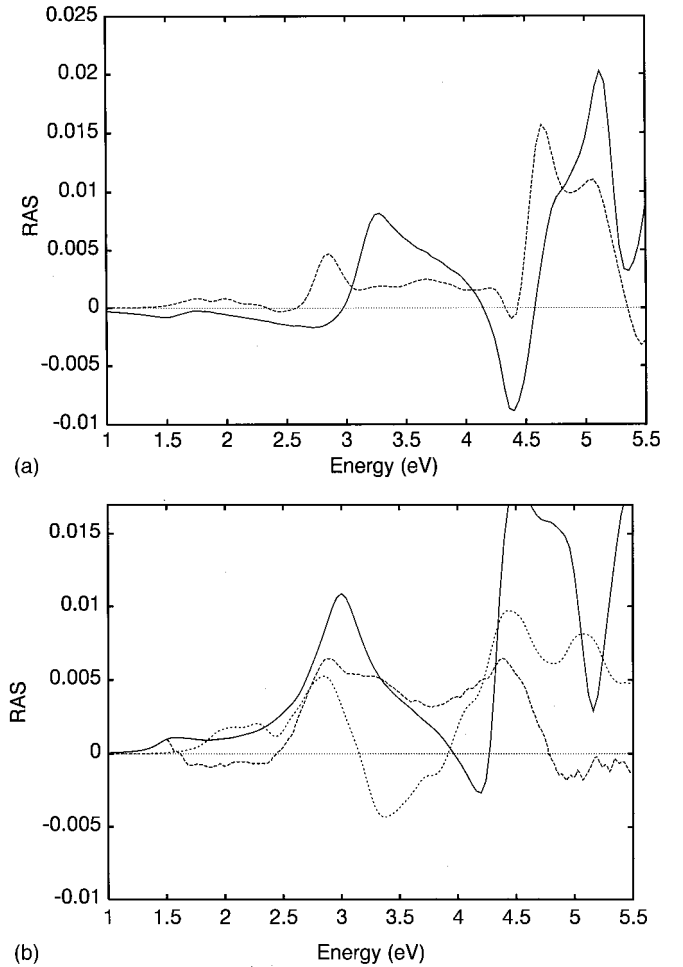


FIG. 5. (a) Full line: GaAs RAS results from the quenching-broadening-shifting model, with the following choice of parameters: $f_x=1$, $f_y=0.5$, $\gamma_x=0.1$ eV, $\gamma_y=\gamma_{bulk}=0.03$ eV, $\Delta\omega_x=\Delta\omega_y=0.1$ eV (see text). Dashed line: microscopic calculation for the (110) slab, with 31 layers and 1024 k points. (b) Dashed line: experimental RAS data for GaAs(100) $\beta 2(2 \times 4)$, from Ref. 17. Dotted line: microscopic calculation for the same surface. Full line: quenching-broadening-shifting model, with the following choice of parameters: $f_x=f_y=1$, $\gamma_x=\gamma_y=0.1$ eV, $\gamma_{bulk}=0.03$ eV, $\Delta\omega_x=-0.1$ eV, $\Delta\omega_y=0$.

hybrid spectrum is rather similar (although energy shifted) to the microscopically calculated RAS spectrum, also shown in Fig. 5(a) (dashed line). For some choice of the parameters we got difference spectra *approximately* bulklike, that is showing peaks close to the two bulk critical-point energies, but, differently from the bulk spectrum, with a negative region in between [Fig. 5(b), full line]. A similar RA spectrum is the result of a realistic tight-binding (TB) slab calculation carried out for another GaAs surface, the (polar) (100) $\beta 2(2 \times 4)$. The calculated RAS is shown in Fig. 5(b), by the short-dashed line, while the experimental spectrum, more similar to the bulk one, corresponds to the long-dashed line.¹⁷ This suggests that the surface-exciton and surface local-field effect may be determinant to yield bulklike surface spectra. A recent calculation for Si(110):H,¹⁸ where the experimental RA line shape is bulklike,¹⁹ shows indeed that the surface local-field effect, treated therein according to the point-dipole approximation, is crucial to obtain a bulklike theoretical line shape.

IV. SUMMARY AND CONCLUSIONS

To summarize, we have shown that surface effects on optical properties of GaAs are localized in a few monolayers below the surface.²⁰ As it has been discussed in Sec. III, these results do not depend explicitly on the particular system considered, suggesting a more general validity, i.e., indicating that for a wide class of semiconductor surfaces the surface effects on optical properties, including the crystal termination effect, are well described using slabs of a few tens of monolayers. In the absence of peculiar features due to surface states, the crystal-termination effect can be phenomenologically modeled as a shift, broadening, and reduction of the bulk spectrum. Many combinations of these parameters yield surface spectra resembling the derivative of the bulk absorption spectrum. It must be emphasized that the amounts of shift, broadening and reduction are ultimately determined by the microscopic structure of the surface; furthermore, these bulk-derived structures coexist with transitions directly involving surface states. After subtraction of individual spectra to obtain RAS or SDR spectra, the resulting line shape can be qualitatively different from a derivativelike line shape, as in the case of GaAs(110). On the other hand, *approximately* bulklike spectra are obtained for some values of the parameters. However, *truly* bulklike spectra can hardly be obtained in terms of the crystal-termination effect, and they did not even occur as results of our realistic slab calculations. Hence, many-body effects like the surface-exciton or the surface-local-field effect, not included in the one-electron theory, seem to be determinant to obtain truly bulklike line shapes.

In conclusion, we agree with Rossow *et al.*³ and with UK (Ref. 4) that some features of surface spectra originate from

transitions across bulk states. Surface termination effects, however, involve a more complex mechanism than that described by UK. In fact, the broadening of the bulk dielectric function near the surface is the most important crystal-termination effect, due to the breaking of k_z conservation at surfaces. It does not imply, however, that photogenerated electrons and holes have shorter lifetimes than in the bulk. This effect yields derivativelike line shapes, as those obtained at many chemically saturated surfaces.

Finally, we would like to stress that many effects concur to determine surface optical properties. It is not possible to interpret optical spectra of all surfaces in terms of a single effect, either the crystal-termination effect, or transitions across surface states. Caution must also be used in assigning spectral features to bulk-state transitions uniquely because of their energy positions, as exemplified by the case of GaAs(110), where we found that the main peak of the calculated spectrum, occurring almost at the same energy as the E_1 bulk feature, contains a substantial contribution of transitions across surface states.

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