

Optical anisotropy induced by cesium adsorption on the As-rich $c(2\times 8)$ reconstruction of GaAs(001)

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(Received 18 July 2003; revised manuscript received 17 November 2003; published 22 March 2004)

Upon adsorption of Cs, the As-rich $c(2\times 8)/(2\times 4)$ reconstruction of GaAs(001) is found to exhibit an intense negative signal between 3 eV and 5 eV in the reflectance anisotropy spectrum. This signal has a universal character in that similar features also appear on the Ga-rich surface. The mechanism of this signal is interpreted using *ab initio* calculations of Cs adsorption at As and Ga sites of the As-rich surface. The calculations succeed in explaining the universality of the signal. In the vicinity of the E'_0 bulk critical point at 4.5 eV, the signal arises from perturbation of bulk states terminating at the surface. At lower energies, the signal arises from the creation of new surface resonances induced by the Cs adatom.

DOI: 10.1103/PhysRevB.69.125332

PACS number(s): 78.40.Fy, 78.68.+m

I. INTRODUCTION

Surface optical techniques, such as reflectance anisotropy spectroscopy (RAS) or surface differential spectroscopy, possess excellent potential for the investigation of surface chemical processes. The focus of interest of such studies lies in the possibility of *in situ* analysis, while the spectroscopic nature of the techniques enables a wealth of information to be obtained. So far, these techniques have been mostly employed in studying the optical transitions of clean, well-characterized surfaces or the various processes involved in heteroepitaxial and homoepitaxial growth. On the other hand, changes of the surface optical spectra caused by adsorption of elements for which the electronegativity strongly differs from that of the substrate atoms have been relatively less investigated. Of the various elements studied, the most frequently considered has been oxygen, the adsorption of which has been shown to quench RA signals on As-rich¹ and Ga-rich² (001) GaAs. Layer-by-layer oxidation of Si(001) has been found to give rise to oscillations in the RAS signal amplitude,³ while the oxidation mechanism of InAs was shown, again using RAS, to strongly depend on surface stoichiometry.⁴ Sulfur adsorption has been investigated, in ultrahigh vacuum⁵ and in a liquid environment,⁶ where the photochemical formation of surface dimers under the protection of a passivating overlayer was demonstrated. Adsorption of electropositive elements has also been studied, such as for hydrogen on GaAs⁷ and on silicon.⁸ Adsorption of alkali metals on GaAs, such as cesium⁹ and sodium and potassium¹⁰ has been investigated with an emphasis on the application of RAS to the study of disorder-order phase transitions under annealing. Such studies are frequently interpreted in a phenomenological manner, as a detailed microscopic understanding of the adsorbate-substrate interaction—not to mention the mechanisms behind the induced RAS changes—is usually lacking.

In this work, we show experimentally that, for the As-rich

$(2\times 4)/c(2\times 8)$ and Ga-rich $(4\times 2)/c(8\times 2)$ reconstructions, Cs adsorption causes the appearance of a very strong negative signal lying between 3 eV and 5 eV. Since quite similar signals are observed for the two reconstructions, and even, as reported independently,¹¹ for adsorption of other alkali-metal atoms, the mechanism underlying the optical anisotropy must be independent of the details of the surface structure. We analyze the Cs-induced changes of the RA spectrum of GaAs(001) using *ab initio* calculations, considering only the As-rich $(2\times 4)/c(2\times 8)$ reconstruction for which both the geometrical properties^{12–14} and the chemistry of the adsorption¹⁵ are known. The calculations succeed in reproducing the observed universality: although the shape of the Cs-induced signal to some extent depends on the site which is populated, these differences are found to be small, for adsorption at two very different sites related to surface arsenic and to surface gallium atoms, respectively. Possible underlying mechanisms for the changes, which originate in subsurface layers, are presented and discussed in detail.

In the following section we present the experimental results of the RAS investigation. The calculation of the Cs-induced effects is given in Sec. III and the results are interpreted in Sec. IV. Overall conclusions are given in Sec. V.

II. EXPERIMENT

We determined, using RAS, the Cs-induced changes of the spectral dependence of $\Delta R/R = (R_{[1\bar{1}0]} - R_{[110]})/R$, where $R_{[1\bar{1}0]}$ and $R_{[110]}$ are the surface reflectivities for light polarized along the corresponding surface orientations. This was performed in a UHV system described elsewhere¹⁶ for which the base pressure lies in the low 10^{-11} mbar range. The RAS system has also been described separately.¹⁷ Cesium adsorption was performed using a thoroughly outgassed getter, in a pressure not exceeding 10^{-10} mbar. The undoped sample was first treated by a HCl isopropanol solution¹⁸ before being annealed to 450 °C. Although no characterization of the surface symmetry was performed using low-energy

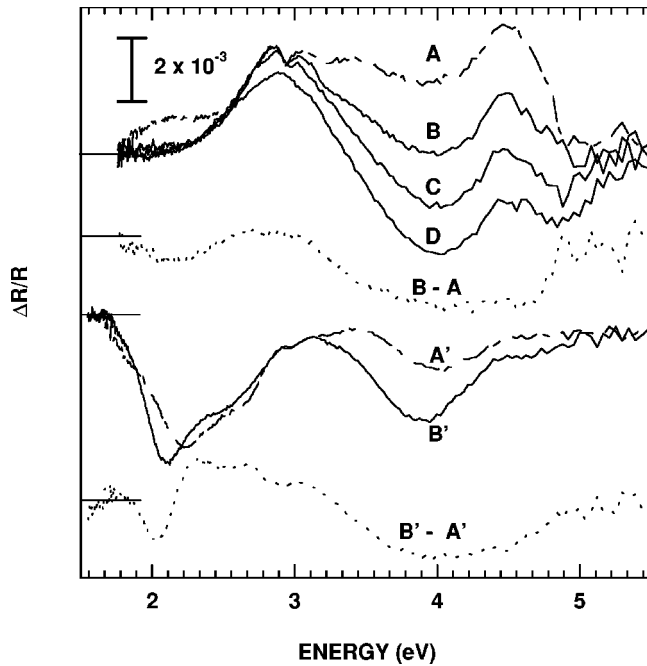


FIG. 1. Top: Experimental reflectance anisotropy spectra for clean (A) and Cs-covered surfaces of As-rich GaAs(001). Spectra B–D indicate coverages of 0.1, 0.2, and 0.3 ML of Cs. Bottom: Spectra for clean (A') and Cs-covered (B') surfaces for the Ga-rich GaAs(001) surfaces.

electron diffraction, RA spectroscopy allowed us to conclude without doubt that, at this stage, the surface exhibited the As-rich surface characterized by a $(2 \times 4)/c(2 \times 8)$ reconstruction. The RA spectrum subsequently taken at RT is shown in Curve A of Fig. 1, and is quite similar to the known anisotropic signature of the latter reconstruction.¹⁹ It exhibits a positive line at 4.5 eV, close to the E'_0 bulk critical point, which has been attributed to bulk-related transitions, whereas the positive signal near 3 eV has been shown to be partly of bulk and partly of surface origin.^{20–22}

Shown in Fig. 1 are the reflectance anisotropy spectra taken at RT after RT adsorption of 0.1 (B), 0.2 (C), and 0.3 (D) ML (monolayer), respectively, of cesium. The main effect of Cs adsorption on the spectrum is to induce a relatively broad negative signal between 3 eV and 5 eV. This signal, shown in more detail at the initial adsorption stage as the difference between curves B and A, may be a composite signal including quenching of the bulk-originating signal at 4.5 eV. The difference signal is very small between 2.5 eV and 3 eV as the line at 3 eV is only affected by Cs adsorption at larger coverages. In addition, a small negative signal is observed near 2 eV in the difference spectrum, which saturates at low coverages.

The Cs-induced signal near 4 eV is remarkable for two reasons. First, this signal is extremely sensitive to slight cesium doses since, with the present signal-to-noise ratio, a coverage as small as 10^{-2} ML should induce a detectable modification. Second, the latter signal seems to have a universal character: we have found that it depends rather weakly on the surface reconstruction, since Cs-induced signals observed for a Ga-rich GaAs(001) surface are only slightly dif-

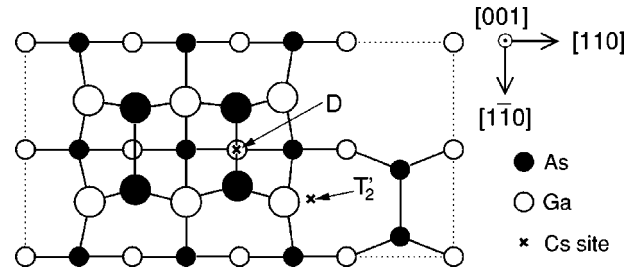


FIG. 2. Schematic diagram of the surface unit cell of the $\beta_2(2 \times 4)$ reconstruction of GaAs(001). Primary adsorption sites for Cs are marked.

ferent. In the lower panel of Fig. 1 we show the spectra of the clean gallium-rich surface (A') and the same surface after RT adsorption of a similar Cs coverage (B'), already shown in a preliminary report.¹¹ Two types of Cs-induced effects are observed. Below 3 eV, the modification is due to the effect of Cs on surface states, as previously reported elsewhere.⁹ In the 3–5 eV energy range, a negative signal also appears in the same way as for the As-rich surface. This signal, shown in the difference spectrum (B'–A'), has a shape and width quite similar to that found on the As-rich surface, and might be of the same nature. Furthermore, similar signals are also found for adsorption of different alkali-metal adatoms at the As-rich and Ga-rich surfaces.¹¹ The main purpose of the present paper is to explain the origin of the Cs-induced signal and of this universality.

III. CALCULATION OF THE RA SPECTRA

The β_2 unit cell of the clean surface is shown schematically in Fig. 2. It features two As dimers at the top layer with a further As dimer situated at the third atomic layer.^{12–14} Gallium atoms with dangling bonds are present in the second layer. The geometry and energetics of cesium adsorption have previously been investigated in Ref. 15 using a combination of density-functional theory–local-density approximation (DFT-LDA) calculations and x-ray diffraction studies. Three dominant adsorption sites were considered in that work: the As-related dimer bridge site D, the gallium dangling bond site, labeled T'_2 , and to some minor extent the T_3 trench site. As expected, the nature of the chemical bond was shown to be quite different for the As-related D site and for the Ga-related T'_2 one: the charge transfer is limited for the negatively charged As site, whereas this transfer is almost complete at the empty Ga dangling bond site. Cs-substrate bonding and related charge-transfer processes influence the surface band structure mainly through the appearance of a partially filled band below the conduction band. It will be shown below that the details of this bonding are not crucial for explaining the Cs-induced changes in the optical properties.

Here, in order to explain the universality of the signal, we compare the calculated Cs-induced changes for the D and T'_2 sites, for which the positions are noted in Fig. 2. The surface was simulated by periodically repeating supercells of thin GaAs slabs (10 atomic layers) separated by vacuum regions about 10 Å thick. Gallium dangling bonds on the back sur-

face were saturated with a layer of fractionally charged ($Z = 1.25$) hydrogen. Structural optimization for the D and T_2' sites was performed at a cutoff energy of 13 Ry and with a single \mathbf{k} point (Γ). The bottom two layers were fixed to the ideal bulk positions, and all other atoms were allowed to relax until the atomic forces did not exceed 35 meV/Å. Norm-conserving pseudopotentials were used for all atomic species; for the Cs atom, these were constructed with special care, treating the whole fifth electronic shell as valence, together with the optical 6s electron. Nonlinear core corrections²³ were used with gallium. As discussed in more detail in Ref. 15, we find that 13 Ry gives a reasonably accurate description of the Cs/GaAs ground state, and eigenvalues are converged by about ± 0.05 eV to those calculated at 17 Ry. The convergence of the calculated optical spectra is hence fully consistent with the accuracy which can be achieved with the used Brillouin-zone sampling and spectral broadening, to be given below.

Ab initio calculations of the RAS spectra of the clean and cesiated GaAs(001) surfaces were performed by calculating the independent-particle response function, again at a cutoff of 13 Ry. For a repeated slab geometry, this is given by the half-slab polarizability, defined by the standard expression

$$\text{Im}\{\alpha_{ii}^{\text{hs}}\} = \frac{\pi e^2}{m^2 \omega^2 A d} \sum_{\mathbf{k}} \sum_{v,c} |p_{v,c}^i(\mathbf{k})|^2 \times \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega], \quad (1)$$

where d is half the slab thickness and $p_{v,c}^i(\mathbf{k})$ is the transition matrix element of the momentum operator between valence- (v) and conduction- (c) band states at wave vector \mathbf{k} and of energy $E(i=x,y,z)$. In practice, we generalize $\text{Im}\{\alpha_{ii}^{\text{hs}}\}$ for any value of d by utilizing a real-space cutoff function in $p_{v,c}^i(\mathbf{k})$ (see Ref. 27 for details). As well as for analysis purposes, this procedure is required to remove the spurious anisotropic contribution from the back surface. Finally, the slab polarizability is related to the normalized reflectivity change with respect to the Fresnel equations by

$$\frac{\Delta R_i(\omega)}{R_0(\omega)} = \frac{4\omega d}{c} \text{Im} \frac{4\pi\alpha_{ii}^{\text{hs}}}{\varepsilon_b - 1}, \quad (2)$$

from which we calculate the reflectance anisotropy, given by

$$\frac{\Delta R}{R} = \frac{\Delta R_x(\omega)}{R_0(\omega)} - \frac{\Delta R_y(\omega)}{R_0(\omega)}. \quad (3)$$

To correct the well-known underestimation of the band gap occurring in DFT-LDA, we incorporated, via the recipe of Del Sole and Girlanda,²⁴ the necessary self-energy effects by a rigid “scissor operator” shift of 0.8 eV, which is a typical value obtained from studies of bulk GaAs.²⁵ This approach has been previously shown to be quite adequate for the clean GaAs(001) surface.²⁶ Corrections, such as local-field and excitonic effects, spin-orbit interaction, have been omitted, and some effects of size quantization on extended bulk states due to the slab approximation probably remain. In computing the surface dielectric function we found that a

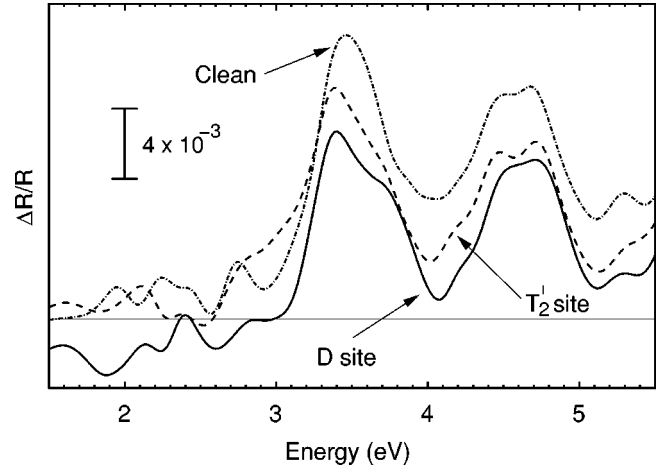


FIG. 3. Calculated RAS spectra of clean and cesiated surfaces. A rigid scissor operator shift of 0.8 eV has been incorporated in the spectra, and a phenomenological Lorentzian broadening of 0.15 eV has been used throughout.

special-point mesh equivalent to 256 \mathbf{k} points in the (1×1) surface Brillouin zone yielded RAS spectra converged to, at worst, 100 meV in the peak positions.

Results are shown in Fig. 3. The calculated RAS spectrum for the clean $\beta 2(2 \times 4)$ surface, being characterized by two main peaks at 3.45 and 4.5–4.7 eV, respectively, is in reasonable agreement with the experimental one, which shows two structures lying at 2.95 and 4.5 eV. There are slight discrepancies mostly concerning the peak at 2.95 eV. The peak position appears at a slightly higher energy than that of the experimental one. This may be due to (i) *computational* approximations, namely, the use of a scissor operator to simulate self-energy corrections, the size-quantization effects, and the use of a limited number of plane waves, all of which are sources of small shifts in the peak positions and (ii) *physical* approximations, mainly the neglect of excitonic, local-field, and spin-orbit effects, which can also influence the strength of the peak (we note that the amplitude of the bulk GaAs E_1 peak is much more sensitive to excitonic effects than that of the E'_0/E_2 peak²⁸). Furthermore, the relative amplitude of the two main peaks is reversed with respect to the experiment. This is probably due to the experimental surface preparation procedure, since the peak at 2.95 eV is known to be strongly influenced by the surface quality. These small differences are not crucial for the understanding of the present results since we are considering the *changes* of the spectra following Cs adsorption.

The spectra for the cesium-covered surfaces, computed for one Cs atom per unit cell, approximately correspond to a coverage of 0.10 ML.³¹ These spectra reproduce and explain the two main experimental observations: within the equivalent energetic region that is most sensitive to Cs adsorption (3.6–4.8 eV) the two sites show a clear reduction in the RAS signal over a broad range, a feature which is weakly dependent on adsorption site. The calculations also reproduce the strong sensitivity of the Cs-induced modifications, since the signal magnitude approaches zero at 4 eV. The theory also predicts a decrease of the RAS signal near 3.5 eV, which

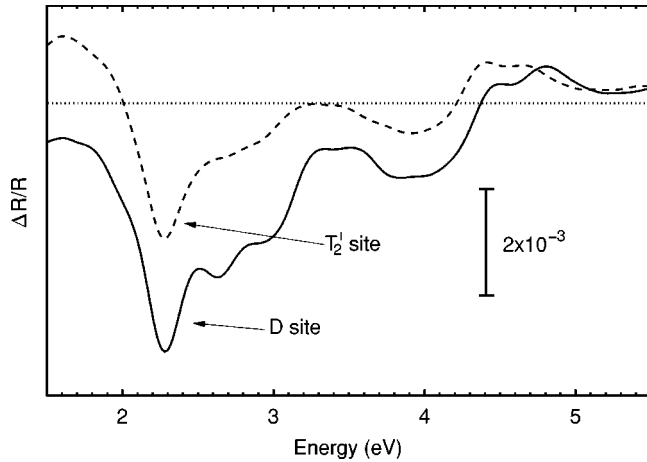


FIG. 4. Contribution to total RAS signal from Cs-induced band for the two cesium-covered surfaces.

corresponds, in the experimental spectrum, to the main structure observed near 3 eV. For the latter line, such a decrease appears to a significant extent in the experiment only for a coverage of 0.3 ML (curve D of Fig. 1); this discrepancy may be due to the experimental underestimation of the amplitude of the 3 eV peak of the clean surface, as mentioned above.²²

IV. DISCUSSION

Alkali-metal adsorption can influence the optical spectrum in several possible ways: (i) changes in surface geometry due to bonding, (ii) introduction of new optically active states (being related to the outer electronic states of the adatoms or to alkali-metal-induced states), (iii) mixing of adatom states with existing surface states [chemical bonding—(iii-A)] or bulk states [surface resonances—(iii-B)], and (iv) perturbation of surface or bulk states, via, for example, changes in surface electric fields (Stark shifts, wave-function polarization) due to charge transfer, or via the presence of the adatom potential.

Among the above mechanisms we can immediately neglect (i) because the alkali-metal-induced surface relaxation, as reported in Ref. 15, is minimal, and hence can only weakly affect the optical spectra. We can also safely exclude a significant contribution to the spectrum of optical transitions from the states involved directly in the bonding. In Ref. 15 it was shown that Cs adsorption induces a partially occupied band, which for T_2' corresponds to a new state [mechanism (ii)] and for D corresponds to a hybridization of the alkali-metal $6s^1$ state and preexisting surface states [mechanism (iii-A)]. The anisotropy signals due to the latter states are isolated in Fig. 4. These states are found to be mainly responsible for a negative signal in the 2.0–3.0 eV range, which is more pronounced for the D site. This signal may correspond to the small negative feature at 2.0–2.5 eV in the A-B experimental spectrum of Fig. 1. Clearly, both of these mechanisms contribute only weakly to the RAS in the 3.6–4.8 eV range.

Furthermore, it can easily be shown that the negative sig-

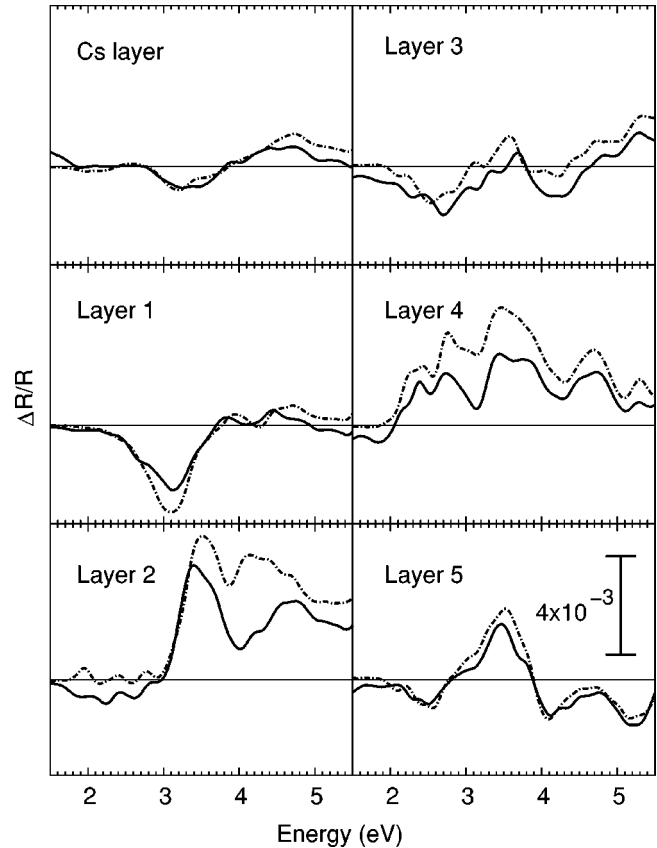


FIG. 5. Layer-by-layer decomposition of the RAS spectra for the clean surface (dot-dashed lines) and for the surface with Cs atoms at the D sites (solid lines) surfaces. Except for the “Cs layer,” which encompasses the Cs atom and some vacuum layers correspond to integer multiples of the bulk interlayer distance.

nal near 4 eV cannot be caused by intrinsic states of the adatom [mechanism (ii)]. In Fig. 5 we present a layer-by-layer decomposition of the RAS spectrum, for clean and D structures, obtained by applying a real-space cutoff function to the optical matrix elements.²⁷ As seen in the figure, there is virtually no contribution from the “Cs layer” (the remaining signal is due to As dimer states spilling out into this region). From the remaining panels of Fig. 5, it appears that the optical transitions responsible for the 4 eV signal occur in the subsurface layers (2–4) rather than deeper in the bulk.

These results imply that the effect of the adatom on the spectrum is *indirect*. The effect of Cs-induced perturbations on the bulk states, according to mechanism (iv), is expected to occur mostly near the E_1 and E'_0/E_2 critical-point energies. In order to verify this point, we considered the reflectance anisotropy model of Del Sole and Onida (DS-O).²⁹ In this scheme, optical anisotropy arising from bulk states terminating at the surface is parametrized by an anisotropic quenching f_i , broadening γ_i , and shifting $\Delta\omega_i$ ($i=x,y,z$) of the bulk dielectric function ϵ_b to yield an anisotropic surface dielectric function $\epsilon_{s,i}$. Taking reasonable values for these three parameters for both clean and adsorbed surfaces (values of $\Delta\omega_i$, for example, can be easily estimated from inspection of the calculated dielectric functions), we found that the model is indeed able to account for reductions in the

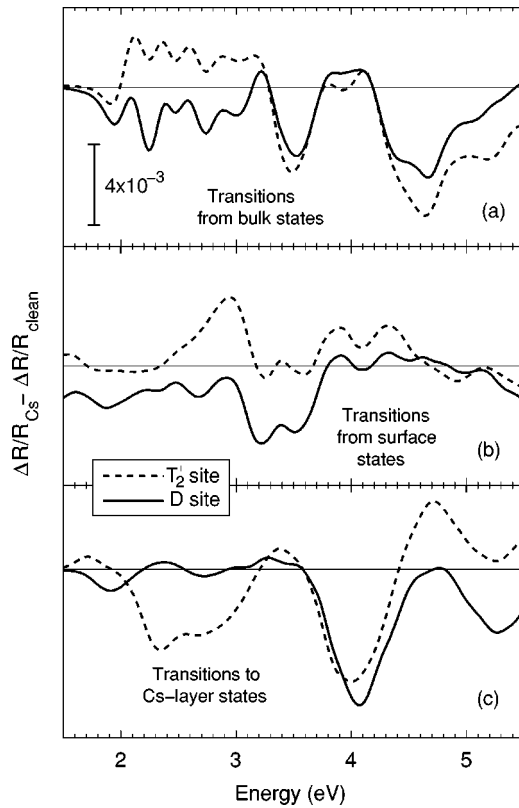


FIG. 6. State-to-state decomposition of the Cs-induced changes of the RAS spectra for the two cesium-covered surfaces. Surface (*s*), bulk (*b*), and Cs layer (Cs) contributions are grouped as follows: (a) $b-s + b-b$, and (b) $s-s + s-b$, and (c) $s-Cs + b-Cs$. Remaining contributions are negligible.

high-energy part of the RAS spectrum, i.e., close to the E'_0 critical point. However, the model is unable to describe the effects of Cs adsorption in the intermediate range between the E_1 and E'_0 energies, i.e., the 3.3–4.3 eV range in the experiment, which hence must derive from true microscopic phenomena.

The origin of the Cs-induced signal near 4 eV and its weak dependence on the surface reconstruction can be understood by categorizing electronic states according to the spatial region in which they are predominantly localized. States are thus labeled as bulk (*b*), surface (*s*), or Cs layer (Cs) states.³⁰ The Cs layer is defined as having a width equal to the calculated ionic diameter of 3.76 Å, while the surface region is defined to include all surface dimers and their back bonds (about four layers thick). We then group the optical transitions, primarily for reasons of clarity, as follows: (a) transitions from bulk states [$b-s + b-b$]; (b) transitions from surface states [$s-s + s-b$]; and (c) transitions to Cs layer states [$b-Cs + s-Cs$]. The remaining contribution, transitions from Cs states [$Cs-Cs + Cs-s + Cs-b$], is practically zero (<0.001) in the energy range of interest.

In Fig. 6 we show the state-to-state decomposition of the calculated Cs-induced *change* in the RAS spectra (i.e., the decomposition of the difference between the Cs-covered surface RAS and the clean surface RAS). This decomposition allows us to distinguish site-independent effects and site-

dependent ones. Site-dependent signals appear in panel (b) for site D and panel (c) for site T'_2 . These signals should account for the observed slight dependence of the Cs-induced signal on the surface reconstruction, and, in agreement with the experimental observations, are relatively small with respect to site-independent signals. Site-independent signals are observed in panel (a) of Fig. 6 at the energy of the E_1 and E'_0 critical points, in agreement with the predictions of the DS-O model. Physically, these signals reflect shifts in the energy of the involved states, as well as changes in their polarization, as caused by the Cs-induced modification of the surface potential [mechanism (iv)]. The strongest site-independent signals are found in Fig. 6(c), at 4 eV (corresponding to the experimental energy of 3.5 eV at which the experimental signal is observed). For the latter signal, more detailed analysis reveals that the isolated *s*-Cs and *b*-Cs components consist of peaks at similar energies and of similar magnitudes. We conclude that the negative Cs-induced change has a double origin: the high-energy side (around 4.5 eV) of the signal originates from perturbations of bulk states terminating at the surface [mechanism (iv)], whereas the low-energy side is due to subsurface transitions to Cs layer states.

We now illustrate the nature of the transition responsible for the low-energy side of the signal. Surface states involved in the *s*-Cs component lie roughly 1 eV below the valence-band maximum and extend quite deeply into the substrate, and are hence more precisely classified as surface resonances. For the *b*-Cs transition, the initial state is not largely influenced by the Cs atom, which is not surprising since the occupied atomlike states on the Cs lie far deeper in energy than the optically active slab states shown. The Cs-related nature of the *final* state of the above transitions seems to be in contradiction with the fact that there is almost no signal from the Cs layer itself (see Fig. 5). In order to resolve this contradiction, we show in Fig. 7 isosurface maps in real space of the initial and final states, respectively, that participate in the strongest *b*-Cs transition around 4 eV, for the case of the D structure. The figure shows that the final state is a type of surface resonance localized primarily on the adatom, but for which only the component of the resonance state localized *within the substrate* is responsible for the optical spectrum. These states are found to be energetically positioned 2–3 eV (DFT-LDA energies) above the valence-band maximum, and are therefore resonant with the conduction band. We term these states “Cs resonances,” and their contribution can be characterized as mechanism (iii-B). Although the Cs resonances show significant localization on the adatom, a weak component can be seen to spread throughout the substrate. We find that the magnitude of the matrix element of the transition roughly correlates with the degree to which the final state is localized in the substrate, and not on the Cs atom. This can easily be understood, because the initial state is localized in the substrate, and because nonvanishing contributions to optical matrix elements can only come from regions where the initial- and final-state wave functions overlap.

The present findings imply that the Cs atom anisotropically perturbs bulk states as they terminate at the surface.

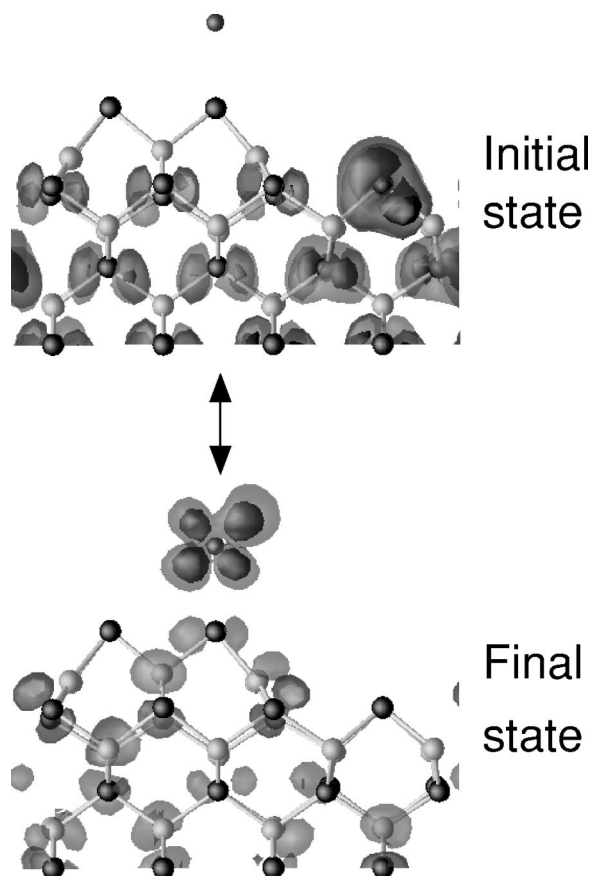


FIG. 7. Isosurfaces of $|\Psi|^2$ for initial and final states involved in the highest probability bulk-Cs transition for Cs adsorption at the D site. The transition energy occurs at $\Delta E = 4.15$ eV. Isosurfaces are shown at $|\Psi|^2 = 0.0015 \text{ bohr}^{-3}$ (darkest), 0.0009 bohr^{-3} , and 0.0003 bohr^{-3} (lightest).

This can be due to two distinct mechanisms. The resonance between bulk states and Cs atomic states is enough to polarize the former states along the $[110]$ direction, which is the direction for which symmetry is broken after adsorption. Another possibility lies in the perturbation of the polarization of

the bulk layer wave functions by the electric field caused by the Cs-induced dipole. Schmidt *et al.*²⁶ have shown, via calculations on GaAs(001): $\beta 2(2 \times 4)$, that the application of a cell-periodic electric field normal to the surface induces RA changes in the RAS signal, quite similar to the changes observed in the current system around 4 eV.³²

V. CONCLUSIONS

We have found that surface optical anisotropy is highly sensitive to the adsorption of cesium atoms. A strong negative signal is observed between 3 and 5 eV. Using *ab initio* calculations, we have found that the signal is composed of two parts, both arising through modifications of *bulk* states. However, the anisotropy caused by the Cs-induced chemical bonds is minimal, and only corresponds to small Cs-induced signals at a lower energy of 2.2 eV.

The lower-energy part of this signal is due to transitions from bulk states or surface resonances to Cs-induced final states. Some of these states have a component that is strongly localized on the Cs atom but which plays a negligible role in the optical response, whereas it is the bulklike part of this wave function which is responsible for the optical transition. Distinct perturbations of the bulk states, due to the presence of the Cs potential, give rise to the high-energy part of the signal, and are responsible for the quenching of the peak in the clean RAS at the bulk E'_0 critical point of 4.5 eV. This general *bulklike* character explains why the anisotropy is similar for the different D and T'_2 sites, and more generally why similar signals are observed on the Ga-rich surface and for different alkali-metal adatoms.¹¹

ACKNOWLEDGMENTS

C.H. acknowledges financial support by the EU through the NANOPHASE Research Training Network (Contract No. HPRM-CT-2002-00167) and from the INFM-PRA project "1MESS." Computer time was granted by IDRIS (Project No. 544). We thank useful discussions with Rodolfo Del Sole, Friedhelm Bechstedt, and Wolf-Gero Schmidt.

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