

***In situ* observation of surface optical anisotropy on InP, InAs, and InSb by chemical modulation spectroscopy**

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In situ observation of surface optical anisotropy due to In dimers in a set of three In-based semiconductor binary compounds—InP, InAs, and InSb—grown by molecular-beam epitaxy is reported. We used an optical reflection technique based on the chemical modulation of the surface, that permits the measurement with light linearly polarized in one selected polarization, usually $[110]$ or $[\bar{1}\bar{1}0]$, typically parallel to the group-III and -V dimers. Spectra for (001) surfaces in the 1–3-eV range were obtained through this technique, and the results are compared to those previously obtained for a set of Ga-based binary compounds, GaP, GaAs and GaSb. For both sets, well-defined features for light polarized along $[110]$ have been observed, that are attributed to transitions between the occupied group-III dimer and the unoccupied dangling-bond bands. [S0163-1829(98)05504-0]

I. INTRODUCTION

Experimental techniques such as reflectance difference spectroscopy¹ or surface photoabsorption (SPA) (Ref. 2) have been reported for the study of the optical properties of the semiconductor surfaces. These techniques have also proved to be a very useful *in situ* characterization tool during growth process in semiconductor technology.³ Despite their technological interest, the interpretation of the spectra is still controversial.^{4–8} Three types of transitions contribute to the surface dielectric constant: surface-surface, bulklike-surface, and bulklike-bulklike. The contribution of the surface-perturbed bulklike states can be very important,⁹ and there is a special need to clarify the origin of the observed features. In the case of III-V compounds, a way to obtain more information about the nature of the observed features is to study the evolution of the experimental spectra from one compound to the other. In the present work we used what we called chemical modulation spectroscopy (CMS), presented in our companion paper,¹⁰ to measure the surface optical properties of a series of In-based binary compounds InP, InAs, and InSb. This technique measures the difference between the reflectance of two surface coverage states, one corresponding to that in which group-V element covers the surface, and the other after a rapid thermal desorption of the group-V coverage, leaving a surface nearly stabilized in a group-III element. This way, we produced a chemical modulation of the surface that allows us to measure the difference in the reflected intensity between these two states, for light linearly polarized along one specific direction, usually $[110]$ and $[\bar{1}\bar{1}0]$, and for energy values ranging from 1 to 3 eV. The results were compared to those previously obtained for Ga-based compounds,¹⁰ and a discussion in terms of transitions between surfacelike states is also presented in this paper.

II. EXPERIMENT

The experimental setup was described elsewhere.¹¹ For each measurement, we grew epitaxial buffer layers on (100)-oriented InP semi-isolating (Fe doped) substrates, sufficiently thick ($\sim 1 \mu\text{m}$) to obtain a relaxed material, and spe-

cial care was paid to obtain a flat surface morphology. We have used beam pulses of P_2 , As_4 , and Sb_4 for InP, InAs, and InSb, respectively, by means of fast-acting, valved-pulsed, solid-source effusion cells. The substrate temperatures used during measurements were $T_s = 370^\circ\text{C}$ for InP, $T_s = 385^\circ\text{C}$ for InAs, and $T_s = 310^\circ\text{C}$ for InSb. These temperatures provide a good desorption rate of group-V atoms from the surface and assure the good quality of the sample, as observed by reflection high-energy electron diffraction (RHEED). The RHEED patterns observed during measurements correspond to the changes in surface reconstruction when a group-V element is deposited and desorbed. For InP, a change between 2×4 and 2×1 was clearly observed when the phosphorus cell was opened. For InAs, the change was from 4×2 to 2×4 , and, for InSb, from 4×2 to 1×3 , when the group-V cell was opened. The beam equivalent pressure (BEP) of the pulses were $\text{BEP}(\text{P}_2) = 2.5 \times 10^{-6}$ Torr, $\text{BEP}(\text{As}_4) = 1.8 \times 10^{-6}$ Torr, and $\text{BEP}(\text{Sb}_4) = 1.8 \times 10^{-6}$ Torr in the case of the measurement on InP, InAs, and InSb, respectively. Pulse lengths were 0.4 s for P_2 and Sb_4 pulses, and 0.3 s for As_4 , and after beam pulses desorption occurred during $t_d = 2$ s for InP and InSb, and 1.5 s for InAs.

III. RESULTS AND DISCUSSION

In order to find a theoretical expression that gives the observed changes in the reflectivity when the last atomic layer is changed, as happens in CMS, we have used a three-layer model¹² (vacuum, surface layer, and bulk), where the changes in the reflectance can be related to the changes in the surface dielectric constant through the expression

$$\Delta R/R = (R_{\text{III}} - R_{\text{V}})/R_{\text{III}} = (-8\pi d/\lambda)(A\Delta\epsilon_{\text{surf}}^i + B\Delta\epsilon_{\text{surf}}^r), \quad (1)$$

where $\Delta\epsilon_{\text{surf}}^r$ and $\Delta\epsilon_{\text{surf}}^i$ are the changes in the real and imaginary part of the surface complex dielectric constant ϵ_{surf} , due to the change in the coverage of the surface, and they are defined by

$$\Delta\epsilon_{\text{surf}}^r = \epsilon_{\text{surf III}}^r - \epsilon_{\text{surf V}}^r, \quad (2)$$

$$\Delta\epsilon_{\text{surf}}^i = \epsilon_{\text{surf III}}^i - \epsilon_{\text{surf V}}^i. \quad (3)$$

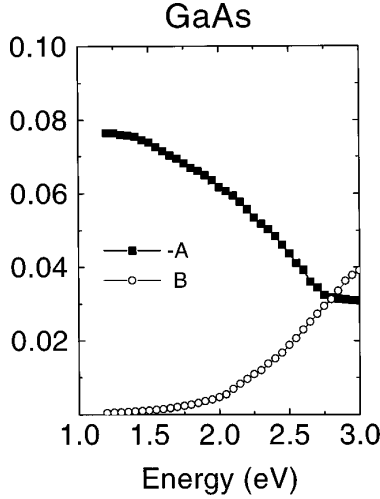


FIG. 1. A and B coefficients for the case of GaAs, obtained from the measured dielectric constant at high temperature using Ref. 13.

d is the thickness of the surface layer, much lower than the wavelength (λ) of the light, and is assumed to be the same for the two surfaces. The coefficients A and B depend on the bulk properties

$$A = (1 - \epsilon_{\text{bulk}}^r) / [(1 - \epsilon_{\text{bulk}}^r)^2 + (\epsilon_{\text{bulk}}^i)^2], \quad (4)$$

$$B = (\epsilon_{\text{bulk}}^i) / [(1 - \epsilon_{\text{bulk}}^r)^2 + (\epsilon_{\text{bulk}}^i)^2]. \quad (5)$$

In Fig. 1 we show the values of A and B for the case of GaAs, obtained from the measured dielectric constant at high temperature.¹³ As it can be observed for this compound, and also for InP and GaP, the changes in the reflectance are mainly related to the changes in the imaginary part of the surface dielectric constant. For InAs, GaSb, and InSb, changes of the real and imaginary part contribute to the changes in the reflectivity. The values of the bulk dielectric constant have been taken from the high-temperature data of Refs. 14–18. We used a simple model to simulate the dielectric constant of the group-III and -V surfaces. For the [110] direction, usually parallel to the In and Ga dimers, we have assumed that the dielectric constant of a surface terminated in element of group III can be modeled with two transitions, one between dimer states located in the energy range between 1 and 3 eV and the other located at much higher energy. The latter simulates the contribution to the dielectric constant of other possible transitions as bulklike transitions, bulklike-surface transitions, etc. The dielectric constant of the surface terminated in element of group V is modeled using only one transition located at much higher energy than 3 eV. For the direction $[1\bar{1}0]$, typically parallel to the group-V dimers, the situation is reversed: the group-V surface is modeled with two transitions and the group-III surface with one. The functional forms used for the transitions are

$$\epsilon_{\text{surf}}^r(E) = I(E_0^2 - E^2) / [(E_0^2 - E^2)^2 + (E\Gamma)^2]^2, \quad (6)$$

$$\epsilon_{\text{surf}}^i(E) = I(E\Gamma^2) / [(E_0^2 - E^2)^2 + (E\Gamma)^2]^2, \quad (7)$$

where I is the intensity of the transition, E_0 is the energetic position, and Γ is the width. Those parameters have been varied to fit the experimental results. By construction the real and imaginary part of the surface dielectric constants are Kramers-Kronig related.

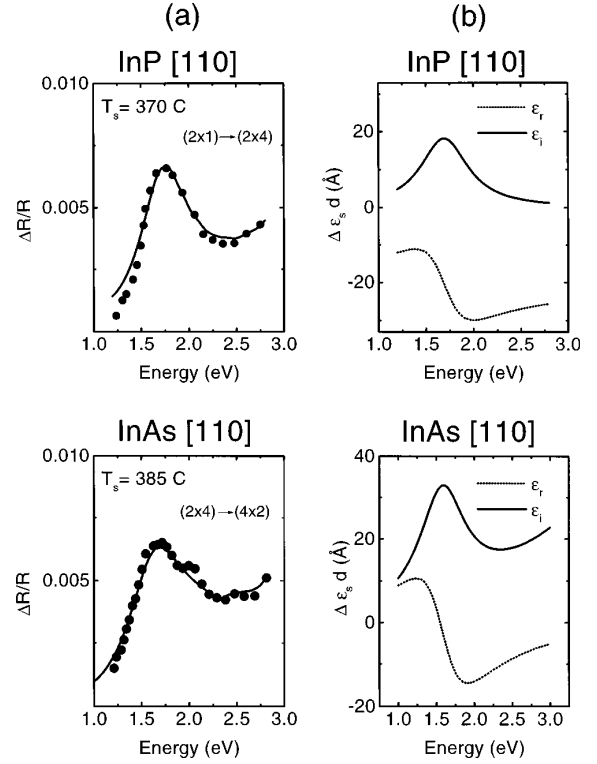


FIG. 2. (a) shows the experimental CMS spectra for InP and InAs (solid dots) for light linearly polarized along the [110] direction, and the theoretical fit (solid line). Also shown is the substrate temperature of the measurement, and the observed change in the reconstruction when the group-V cell is opened. (b) shows the real and imaginary parts of the surface dielectric constant used for the fit, using Eq. (1) and Refs. 14 (InP) and 16 (InAs).

Figure 2(a) shows the experimental CMS spectra for InP and InAs for light linearly polarized along the [110] direction, usually parallel to the In and Ga dimers, and the calculated changes in the reflectivity. Those theoretical estimations were obtained using the dielectric constant given in Fig. 2(b), obtained as already discussed, and using Eq. (1). In Fig. 3 we present the same result for GaP and GaAs. A good agreement is obtained using this simple model for the dielectric constants, which strongly suggests that the main contribution to the spectra comes from states localized in the In (or Ga) surface. We associate the peaks to the transition between the dimer state and the dangling-bond state of In and Ga dimers.

For the $[1\bar{1}0]$ direction, typically parallel to the group-V dimers, such a simple model of the dielectric constants does not give the same good results as for the [110] direction. This can be observed in Fig. 4(a), where we present the experimental and expected changes in the reflectivity using the dielectric constant shown in Fig. 4(b), which corresponds to the best fit obtained using this simple model (GaP does not show relevant features). It is clear that the experimental changes in the dielectric constant cannot be modeled with simple optical transitions related to group-V dimers. Moreover, very recent experiments⁶ showed that the transition attributed to As-As dimers in GaAs could have other bulklike surface-terminated effects. In that case, the changes in the dielectric constant could be more complicated than those assumed here (i.e., the chemical modulation of the surface could produce a modulation in the energy of the transition or

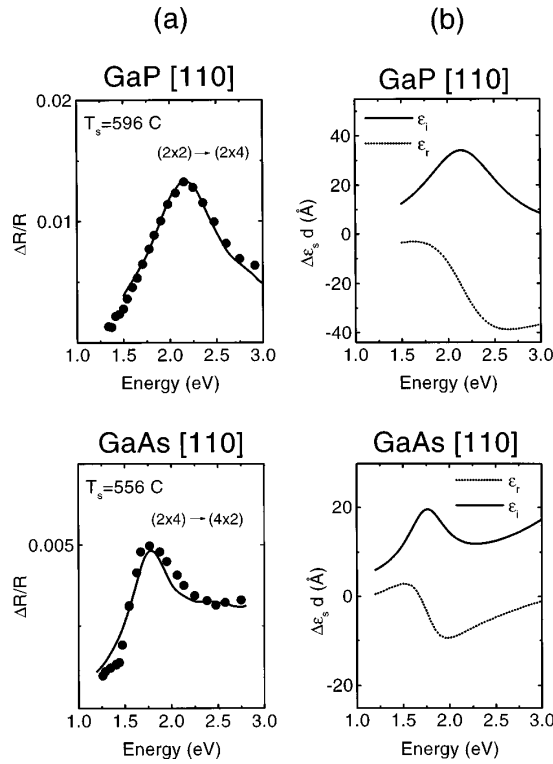


FIG. 3. Experimental CMS spectra for GaP and GaAs (solid dots) for light linearly polarized along the [110] direction, and the theoretical fit (solid line). (b) shows the surface dielectric constant obtained through Refs. 15 (GaP) and 13 (GaAs).

in the lifetime of the state, producing a derivativelike spectra rather than an absorptiolike spectra).

The changes in the reflectivity of the Sb-related compounds are much lower than those of As and P compounds. The spectra in the [110] direction show clearly negative peaks in the change of reflectivity [Fig. 5(a)]. Such peaks could be attributed to transitions between Sb dimer states. For the orthogonal direction the agreement between the experiment and the expected change of the reflectivity is worse, as shown by Fig. 6(a), which clearly suggests that other effects rather than electronic transitions in dimers play an important role in the change of the reflectivity.¹⁹

In the spectral range studied and for the [110] direction, the main contribution of the GaAs, GaP, InAs, and InP spectra comes from surface-surface transitions. In a similar way as we did with the Ga-based compounds,¹⁰ we attribute the observed peak to transitions between dimer and dangling bond states ($d-l^*$).⁴ The energy position of this transition follows the expected behavior: the wave functions of the dimer and dangling-bond states have a strong p -orbital component; therefore, the evolution of the energy of the transition from GaP to GaAs (or InP to InAs) should follow the effective interaction between the p orbitals of the anions and cations. Such an effective interaction between anions and cations can be expressed in terms of optical gaps.^{20,21} These gaps account for the relative position of the atomic levels of the anion and cation and the interaction between the wave function of those levels. For example, the intensity of the effective interaction between p -like orbitals is proportional to the difference in energy between $(\Gamma_7^c/3 + 2\Gamma_8^c/3)$ and $(\Gamma_7^v/3 + 2\Gamma_8^v/3)$. In Fig. 7 we present the experimental energy

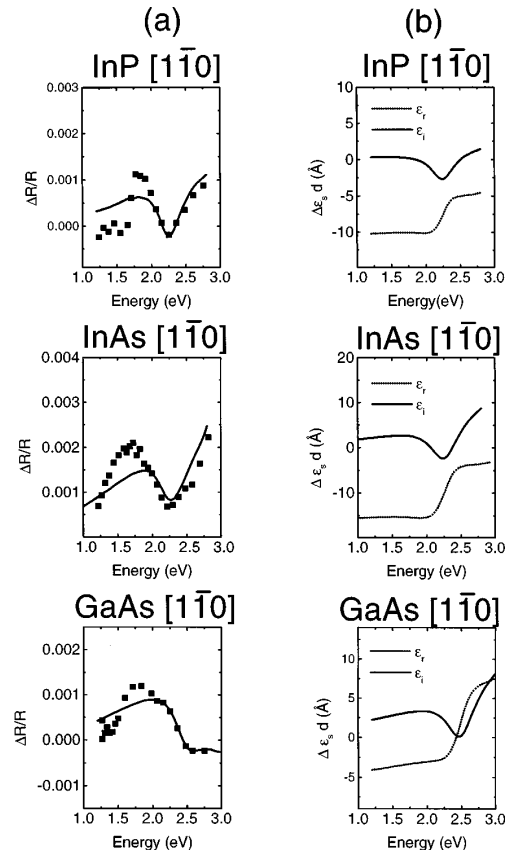


FIG. 4. (a) Experimental CMS spectra obtained for InP, InAs, and GaAs (solid squares) for light linearly polarized parallel along the [110] direction, and the theoretical fit (solid line) obtained using the surface dielectric constant shown in (b).

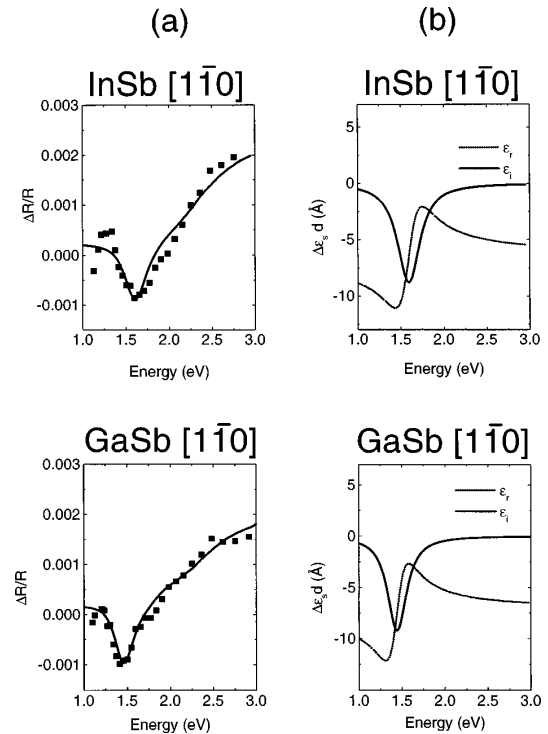


FIG. 5. (a) CMS spectra obtained for InSb and GaSb (solid squares) for light linearly polarized parallel along the [110] direction, and the theoretical fit (solid line) obtained using the surface dielectric constant shown in (b).

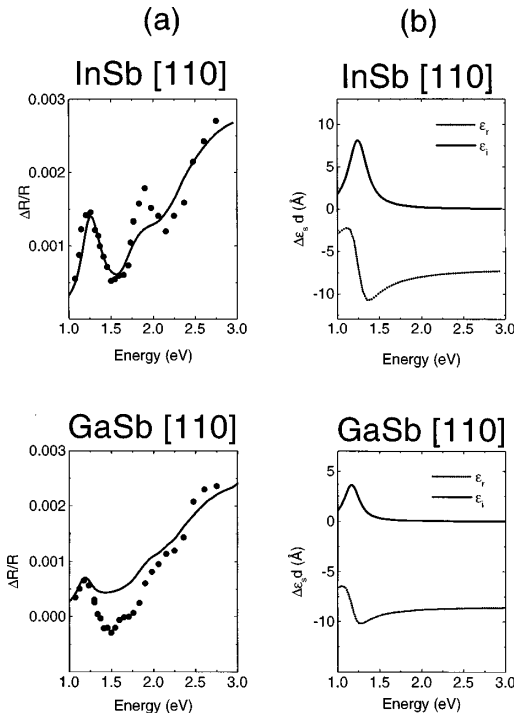


FIG. 6. (a) CMS spectra obtained for InSb and GaSb (solid dots) for light linearly polarized parallel along the [110] direction, and the theoretical fit (solid line) obtained using the surface dielectric constant shown in (b).

position of the $d-l^*$ transition as a function of this effective $p-p$ interaction for the different compounds and as it can be observed, the experimental results follow such evolution. In this figure we also included the position of the first peak observed in the CMS spectra of GaSb and InSb which we attribute also to a $d-l^*$ transition.

Few experimental data for comparison are available in the literature. InP(001) layers prepared by metal-organic vapor-phase epitaxy and measured by the SPA technique²² have been reported to present an In-dimer-related transition at about 630 nm (~ 1.9 eV) and a P-dimer transition about 430 nm (~ 2.8), that are far from our measurements. An InAs(001) surface prepared by molecular-beam epitaxy has

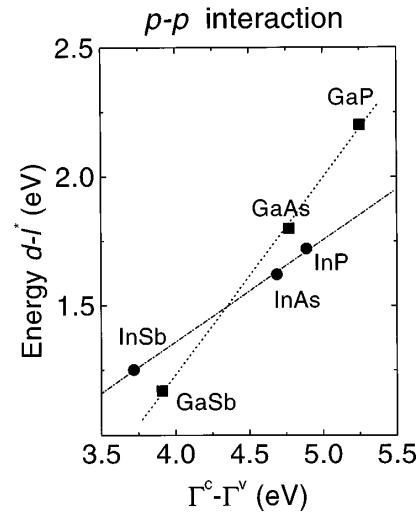


FIG. 7. Experimental energy of the $d-l^*$ transition (circle and square dots) as a function of the effective $p-p$ interaction for the different compounds. The points for GaSb and InSb correspond to the position of the peak with lowest energy in the CMS spectrum.

been measured by reflection anisotropy spectroscopy,²³ showing predominant features near ~ 1.6 eV in the In-rich 4×2 reconstruction at 410 °C and at ~ 2.2 eV in the As-rich 2×4 reconstruction at 350 °C, that are closer to those presented here.

In summary, we used CMS technique for the *in situ* observation of the surface optical anisotropy in two sets of III-V binary compounds. The observed features are related in part with transitions associated to group-III and V dimers, but other bulklike effects can be observed. We performed a simple calculation to fit the experimental spectra to the expected optical transitions, taking in account the temperature dependence of the bulk dielectric constants. These transitions, which are observed in most of the compounds, are well defined, and they can provide useful information about the surface chemistry and optical properties of these compounds during epitaxy and other related technological processes.

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