

In situ optical spectroscopy of Ga dimers on GaP, GaAs, and GaSb by surface chemical modulation

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The optical characterization of the surface anisotropy of three Ga-based semiconductor compounds using an *in situ* technique based on the chemical modulation of the surface is described. In this technique, the anisotropic optical reflectivity is modulated by a periodic variation of the surface stoichiometry using valved pulsed cells for group-V elements (As, P, Sb). The substrate is maintained at sufficiently high temperature in order to obtain rapid desorption of group-V molecules from the surface during flux interruptions. Linearly polarized light, reflected at near normal incidence by the sample, is collected separately along one of the two principal axes of the crystal, [110] and $[1\bar{1}0]$. The change in the surface coverage induces a change in the intensity of the reflected light, and the normalized variation $\Delta R/R$ is recorded as a function of wavelength. Spectra for (001) surfaces in the 1–3 eV range have been obtained with this method for a set of Ga-based binary III-V compounds GaP, GaAs, and GaSb, showing well-defined features for light polarized along the [110] direction, parallel to Ga dimers. These observed maxima are attributed to transitions between the occupied Ga dimer and the unoccupied dangling bond bands, at characteristic energies in each material. [S0163-1829(97)00536-5]

I. INTRODUCTION

Optical reflection has been widely used to the *in situ* study of semiconductor surfaces and to monitor surface structures during epitaxial growth. Previous work in surface optical analysis has been done using polarization-modulated techniques.¹ Reflectance difference spectroscopy (RDS) (Ref. 2) and surface photoabsorption (SPA) (Ref. 3) are the two most commonly used optical techniques to provide information on dielectric responses and growth mechanisms of surfaces and interfaces. RDS is used to measure the difference between normal-incidence reflectances for light polarized along the two principal axes in the surface. On the other hand, SPA measures the change in reflectance caused by surface modification using *p*-polarized light impinging on the surface at the angle of incidence close to the pseudo-Brewster angle of the substrate. A great variety of semiconductor surfaces such as Si,⁴ Ge,⁵ GaAs,^{6–8} InAs,⁹ InGaAs,¹⁰ or AlAs (Ref. 11) grown by molecular beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD) have been studied *in situ* by means of these methods, providing useful information about the surface structure and growth processes of such materials.

We present a technique for the *in situ* study of the surfaces of III-V compounds based on the chemical modulation of the surface coverage. This technique has been applied to the measurement of the optical surface anisotropy of three Ga-based compounds grown by MBE at two crystallographic directions [110] and $[1\bar{1}0]$ and it seems valid for the surface characterization of all III-V compounds, showing optical features that, to our knowledge, have not been observed, except for GaAs, until now.

II. EXPERIMENTAL

Light from a halogen lamp was passed through a heatable viewport used for pyrometric measurements and directed

onto the substrate at near normal incidence. A heated viewport ($T > 450^\circ\text{C}$) was used to avoid deposition of the group-V element during measurements. Reflected light was then passed through a polarizer whose transmission axis was parallel to one of the principal axes of the substrate, which was at an angle of 45° from the horizontal axis. This reflected light was focused by means of a lens and collected by a Si or GaInAs *p-i-n* photodiode mounted on the exit slit of a 0.22 m focal-length monochromator. The change in optical reflectivity with changing surface coverage during deposition and posterior desorption of the group V element molecules was dc amplified and recorded by computer. GaP and GaAs epitaxial buffer layers were grown on (001) oriented GaP and GaAs substrates, respectively, by MBE. GaSb was also grown on (001) GaAs substrate with sufficient thickness ($\sim 1\ \mu\text{m}$) to obtain a flat morphology and relaxed material. Pulses of As_4 , P_2 , and Sb_4 were obtained using valved pulsed cells and solid sources. The substrate temperature was high enough in each case as to permit rapid desorption ($t_d < 3\text{s}$) of group-V element molecules from the surface. The corresponding surface reconstruction changes were monitored by reflection high-energy electron diffraction (RHEED). Figure 1 shows $\Delta R/R$ versus time for As_4 pulses over GaAs for different wavelengths and with the polarizer parallel to the [110] direction. The beam equivalent pressure (BEP) of As_4 is 4×10^{-6} Torr and the pulse length is 0.3 s, with a constant substrate temperature $T_s = 556^\circ\text{C}$. The initial stage (As off) RHEED pattern corresponds to a (4×2) Ga-stabilized surface, and the initial level of reflected light intensity is arbitrarily fixed as R_{Ga} . When the As_4 cell is open (As on), the intensity of reflected light decreases to reach R_{As} , where surface saturation in As occurs. A clear RHEED change is observed, showing a (2×4) diffraction pattern at this moment. After that, the As_4 beam is interrupted (As off) and desorption of As from the surface occurs. The intensity of light increases exponentially with time until the initial level of

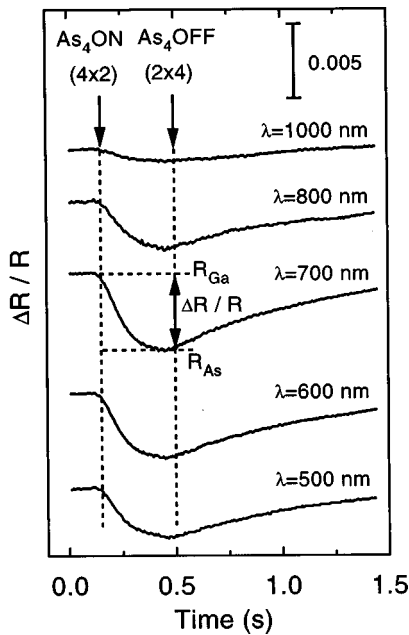


FIG. 1. Time evolution of [110] polarization reflectivity of GaAs during and after each As_4 pulse for various wavelengths. The pulse length is 0.3 s, and the normalized change in the reflectivity is marked as $\Delta R/R = (R_{\text{Ga}} - R_{\text{As}})/R_{\text{Ga}}$. The substrate temperature ($T_s = 556^\circ\text{C}$) needs to be sufficiently high to quickly achieve a fully desorbed (4 \times 2) surface state after As_4 is switched off.

intensity is recovered, and a RHEED (4 \times 2) pattern is observed again. We define the increment in the reflectivity caused by the change in the coverage ΔR as $\Delta R = R_{\text{Ga}} - R_{\text{As}}$ and its normalized value, $\Delta R/R = (R_{\text{Ga}} - R_{\text{As}})/R_{\text{Ga}}$. The maximum $\Delta R/R$ value is $\cong \frac{1}{500}$ and since the recorded signal is quite noisy, the deposition-desorption process is repeated for each wavelength (about 20 times is sufficient) and the signal averaged until mean quadratic standard deviation of ΔR is lower than a fixed value (usually 5%). $\Delta R/R$ is recorded in that way as a function of wavelength in the 1–3 eV (400–1200 nm) range for both selected polarizer azimuths [110] and [110].

III. RESULTS

Figure 2 shows the spectra measured for GaP, GaAs, and GaSb. The substrate temperatures used for measurements were $T_s = 598^\circ\text{C}$ for GaP, 556°C for GaAs, and 462°C for GaSb, where a rapid desorption of group-V molecules from the surface was observed by RHEED, showing the change in the surface reconstruction from (2 \times 4) to (2 \times 2) in GaP, (4 \times 2) to (2 \times 4) in GaAs, and (1 \times 3) to $c(2\times 6)$ in GaSb when the group-V element cell is open. Pulses with a BEP amplitude of 2.5×10^{-6} Torr for P_2 in GaP, 4×10^{-6} Torr for As_4 in GaAs, and 1.7×10^{-6} Torr for Sb_4 in GaSb were used, with pulse lengths of 0.5, 0.3, and 0.5 s, respectively. After the group-V element cell is shutdown, desorption occurs during a time $t_d = 2.5$ s for GaP, 2.2 s for GaAs, and 2.5 s for GaSb.

Well-defined maxima appear in the [110] direction, parallel to Ga dimers. These maxima are located at ~ 2.2 eV (570 nm) for GaP, ~ 1.8 eV (700 nm) for GaAs, and ~ 1.2 eV (1050 nm) for GaSb. In the case of GaAs, the energy posi-

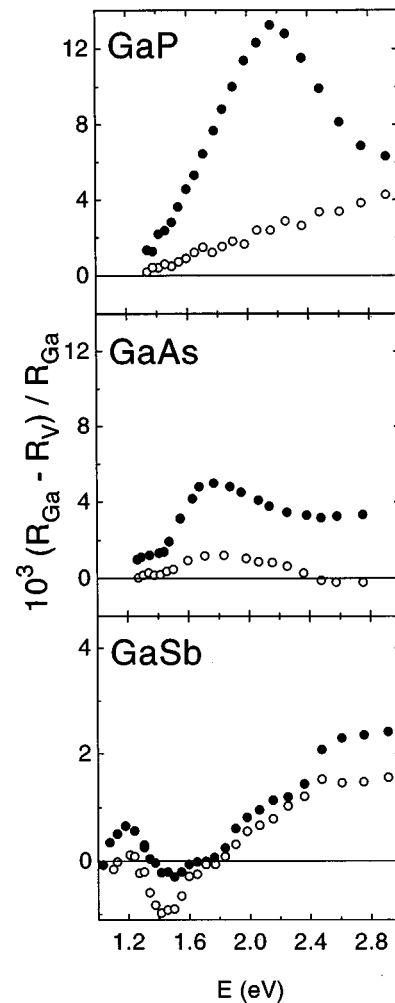


FIG. 2. Spectra for GaP, GaAs, and GaSb. Solid dots are for [110] polarization whereas open dots are for [110]. Substrate temperatures during measurement were $T_s = 598^\circ\text{C}$ for GaP, 556°C for GaAs, and 462°C for GaSb.

tion agrees well with that observed by Aspnes *et al.*¹² at 1.8 eV and assigned to an optical transition between the occupied Ga-dimer and unoccupied dangling-bond bands.¹³ Our technique establishes the difference of reflectivity between two surfaces, covered by group-III and group-V elements, respectively. In this polarization, and in the measured spectral range, surfaces terminated in group-V element are not expected to have abrupt optical features.¹³ By means of the expressions that yield the intensity of the reflected light by a thin film¹⁴ and according to the behavior of the dielectric function of the bulk material by Aspnes *et al.*,¹⁵ we obtain that $\Delta R/R$ is mainly related with the imaginary part of the surface dielectric function that represents the surface absorption. For these reasons, we assign the maxima to be due to transitions between occupied Ga-dimer bands and unoccupied dangling-bond bands at characteristic energies in each material. Moreover, a simple calculation based on a tight-binding (TB) model with interactions up to the first neighbors and an sp^3s^* basis, for a schematic Ga-dimer molecule with a geometry similar to the atomic surface arrangement, shows the same observed tendency (3.09 eV for GaP, 2.98 eV for GaAs, and 2.49 eV for GaSb) for the shift in energy of the maximum with the material. The TB parameters for

the bonds between Ga and P, As, and Sb, were taken from Ref. 16 and the Ga-dimer interaction parameters are taken from the As-dimer interaction parameters of Ref. 17 scaled according to Harrison's $1/d^2$ rule.¹⁸ In this calculation we have assumed that the Ga-Ga distance does not change from one compound to another, being twice the covalent radius of the atomic Ga, whereas the distance between Ga and the group-V atom bonded changes from one compound to another, according to the lattice parameter. This calculation also explains the decrease in the intensity of the transition as the lattice parameter of the compound increases. The calculated energies for the transitions are higher than the experimental ones. Part of this discrepancy can be attributed to the use of TB parameters that correspond to a fit of the 0 K band structures whereas the experiment is done in the 700–800 K range. Also the effective Ga-Ga distance could be lower than twice the covalent radius of Ga, further reducing the transitions energies. In the $[\bar{1}10]$ direction, that is, parallel to group-V dimers, the signal is much lower than in the $[110]$ direction, and no clear deeps have been found except for GaSb, at an energy of ~ 1.4 eV (850 nm). This peak is assigned to a transition from the occupied lone-pair band to the unoccupied Sb dimer band. Probably another peak exists for GaAs near 2.7 eV, as has been observed previously,¹² and at

higher energies inside the uv range for GaP, all related with these kinds of transitions.

In summary, we have applied an optical characterization technique based on the chemical modulation of the surface to obtain spectroscopic information on reconstruction associated surface states on III-V compounds. Well-defined features have been found for GaP, GaAs, and GaSb in the 1–3 eV range for light polarized along $[110]$ direction, parallel to the Ga-Ga dimers. For the case of GaAs, the position of the peak agrees with previous measurements by conventional RDS. The shift in peak position with changing anion (GaX; X=P, As, Sb) shows the strong influence of the group-V chemical bond on the absorption energy of the Ga-Ga dimer of materials. This has been assigned to a transition between bonding Ga-dimer orbitals and empty lone-pair states, and has been observed, as far as we know, for the first time in these compounds.

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