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GaAs(001)-$c(4\times4)$: A chemisorbed structure

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We have carried out an experimental study of the As-stable GaAs(001)-$c(4\times4)$ reconstruction using a combination of molecular-beam epitaxy with reflection electron diffraction, angle-resolved photoemission, and surface-sensitive core-level photoemission. (The measurements were performed at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris—Sud, F-91405 Orsay, France.) Apart from the surface symmetry, the electron-diffraction data show one-dimensional disorder along the [110] direction, probably corresponding to a corrugated-sheet structure in reciprocal space. Photoemission from surface states having dangling-bond character shows a onefold periodicity and an energy dispersion of 0.65 eV along [110], while along [$\bar{1}$10] the dispersion is much smaller, but there is a doubling of the periodicity. Observations of the As 3*d* and Ga 3*d* core levels show a surface As 3*d* component at 0.62 eV higher binding energy than the bulk component, indicative of As—As bonding. The Ga 3*d* surface core-level shift is very small and the line shape is similar to that from the (2×4) surface. The experimental results can be understood on the basis of an As overlayer structure, for which we propose specific models derived from trigonally bonded chemisorbed As.

I. INTRODUCTION

The application of molecular-beam—epitaxy (MBE) techniques[1] make it possible to prepare a wide range of clean, damage-free, reconstructed surfaces of III-V compound semiconductors, which can then be examined *in situ* to evaluate their composition and their crystallographic and electronic structure. The (001) surface of GaAs prepared in this way has been investigated in most detail using Auger-electron spectroscopy[2] (AES), reflection high-energy electron diffraction[3–5] (RHEED), work-function measurements,[6] electron-energy-loss spectroscopy,[6] and photoemission measurements.[7–11]

The different reconstructions of this surface are related to its variable stoichiometry, and several attempts have been made to determine the effective As coverage as a function of the particular reconstruction.[2,9] The most stable structure is the (2×4) [or $c(2\times8)$] reconstruction, where it has been shown previously[4] that the uncertainty about its precise symmetry occurs because the appropriate half-order Laue-zone features for the $c(2\times8)$ structure have not been unequivocally observed in RHEED, although they are quite apparent in some low-energy electron diffraction (LEED) observations. It is generally agreed that both the (2×4) [$c(2\times8)$] and the $c(4\times4)$ structure are As rich, with the latter having the higher As coverage, but there is some discrepancy between Auger spectroscopy[2] and core-level photoemission intensity data[9] as to the actual coverages. In addition, Massies *et al.*[6] observed a reduction of 0.3 eV in the work function of the $c(4\times4)$ surface with respect to the (2×4), and there are also significant differences in the valence-band-related photoemission spectra of these two As stable surfaces.[7]

There have been a few theoretical calculations of the surface electronic structure of ideal, unreconstructed GaAs(001)-(1×1) surfaces[12–14] and of reconstructed surfaces.[11,15] For the (2×4) structure a comparison between theoretical and experimental results gives strong evidence for the presence of asymmetric As dimers in the surface layer.[11] An energy-minimization approach for the $c(4\times4)$ surface based on the assumption that this surface is stoichiometrically As terminated suggests an equal number of symmetric and asymmetric As dimers.[15]

The GaAs(001)-$c(4\times4)$ structure can be observed during MBE growth of GaAs under rather extreme conditions of low temperature and high As flux, but it is usually produced by cooling down a surface showing a (2×4) reconstruction in a flux of arsenic (As_2 or As_4).[4] In this paper we present RHEED, synchrotron radiation excited angle-resolved photoemission (ARPES), and core-level photoemission intensity results that are consistent with the $c(4\times4)$ surface being produced by As chemisorption on the (2×4) structure; i.e., it should not be considered as an intrinsic GaAs surface. We propose a structural model for the chemisorbed state.

II. EXPERIMENTAL PROCEDURES

The RHEED measurements presented in Sec. III were carried out in a MBE system, which has been described in Ref. 4. RHEED patterns were recorded during growth as well as under static conditions with the substrate at room temperature. The primary electron-beam energy was typically 8 keV, at a grazing incidence $\leq 2°$.

The angle-resolved photoemission spectra were obtained using a system we have described previously, which was attached to a toroidal grating monochromator[16] on the A61 beam line at the ACO storage ring at the Laboratoiré pour l'Utilisation du Rayonnement Electromagnétique (LURE), Orsay, France. In addition to an electron-energy analyzer the system contains four Knudsen sources for *in situ* growth of GaAs and metal overlayers and a RHEED facility (5 keV) to monitor the reconstruction behavior. Spectra in the valence-band energy region were taken with an energy resolution of 0.2 eV or better and an angular resolution of 2° (full cone). The spectra were corrected for a smooth background arising from inelastically scattered electrons produced by second- and higher-order diffracted radiation from the grating by the procedure described in Ref. 11. The core-level measurements were taken with similar energy and angular resolutions. The incident radiation was mixed *s-p* polarized (45° or 55° angle of incidence).

Surfaces to be studied were prepared by growth on chemically polished GaAs(001) substrate surfaces using conditions to produce first a (2×4) reconstruction [substrate temperature 790–820 K, As_4 to Ga flux ratio (3–6):1]. The $c(4\times4)$ structure was obtained by cooling the (2×4) reconstructed surface in an As_4 flux to about 700 K (in the range 670–720 K). The photoemission measurements were made after further cooling to room temperature with the As_4 flux turned off, while RHEED patterns could be obtained at any stage of the process.

Alternatively, the various surface structures were obtained using an As_2 flux produced from a two-zone Knudsen cell, which we have referred to previously.[17] The other growth parameters were similar to those used with As_4.

As a reference for the determination of the position of the valence-band maximum, we have used the known binding energy[18] of 18.60 eV for the Ga $3d_{5/2}$ core level. We have also found that a strong feature occurring at -4.9 eV initial energy in the GaAs(001) bulk valence-band spectra at $h\nu=29$ eV and normal emission provides a useful additional check.

III. RESULTS

We will present our results for the GaAs(001)-$c(4\times4)$ structure under three separate headings: RHEED, surface-state emission in the valence-band region, and core-level (Ga $3d$ and As $3d$) measurements. In Sec. IV we will show that they are all consistent with a particular surface model.

A. RHEED data

A set of typical patterns taken in various azimuths, with the substrate at 300 K, is shown in Fig. 1. It is immediately clear from the three low-index azimuth patterns [Figs. 1(a)–1(c)] that the surface has a $c(4\times4)$ structure and this symmetry is maintained over a wide range of As exposure. There is, however, a considerable amount of additional information present in both these and the intermediate azimuth patterns [Figs. 1(d)–1(g)]. The $[\bar{1}10]$ azimuth [in which $\frac{1}{4}$-order features would be observed for a (2×4) reconstruction] shows a high background, while diffuse broad streaks, which are slightly curved, are present in certain other azimuths, particularly [010] and [120]. We have previously suggested,[5] as have others,[19] that this curvature can result from one-dimensional disorder in a

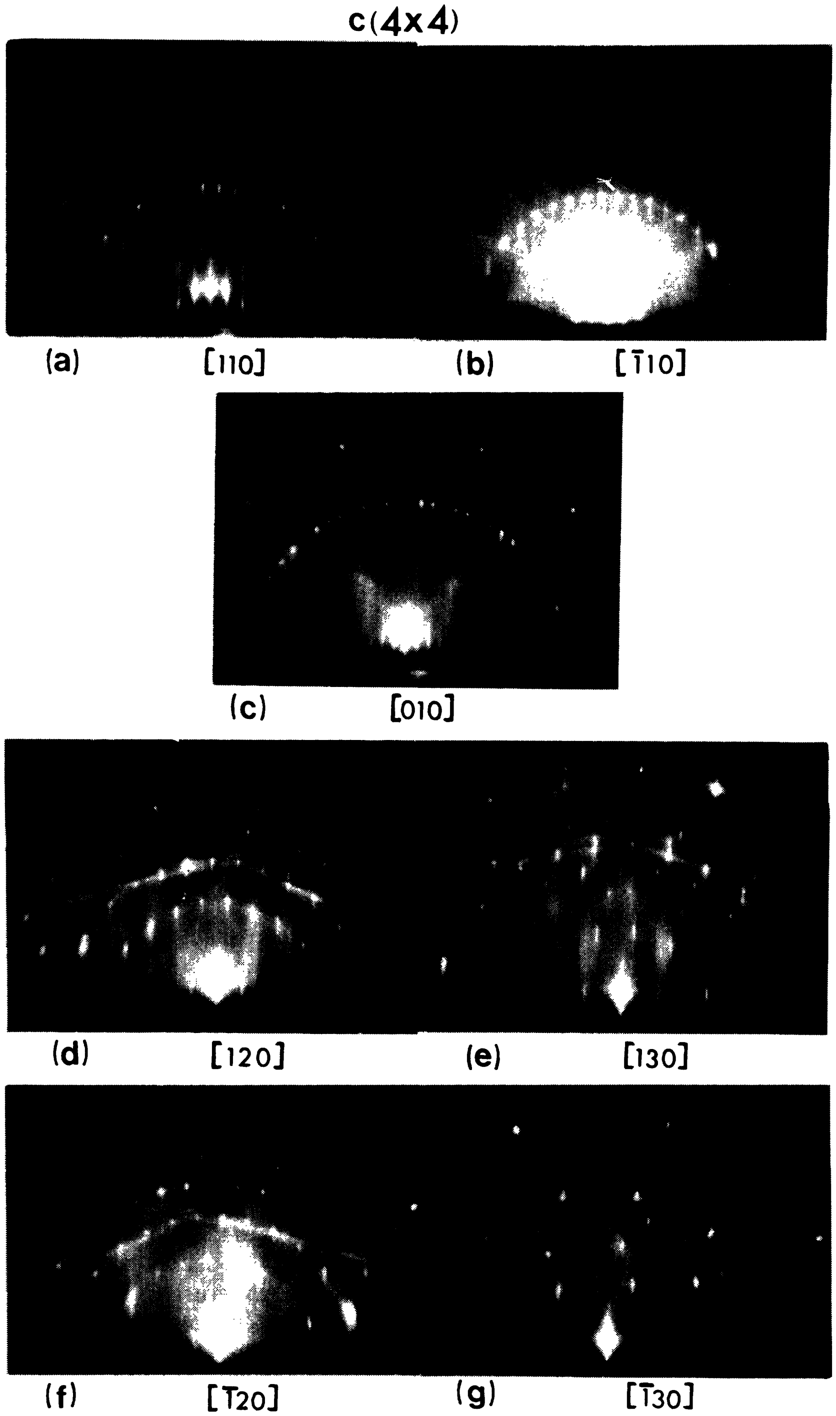

FIG. 1. RHEED patterns for various azimuths of GaAs(001)-$c(4\times4)$.

direction inclined to that of the incident beam. The Fourier transform of this one-dimensional disorder produces planes ("sheet structures") in reciprocal space, which are inclined with respect to the plane of incidence. In this case, however, the reciprocal-lattice sheet structure is not simple, and a compilation of data from several intermediate azimuths leads us to propose the type of corrugated structure shown by the solid lines in Fig. 2, which is a reciprocal-lattice section of the $c(4\times4)$ reconstruction. The broken lines represent Ewald sphere projections, which are approximated by planes for clarity (reasonable at the high energies used in RHEED), and show the intersections with the reciprocal lattice over the range of azimuths used. The corrugated-sheet structure then appears to be consistent with most of the features in the patterns: (i) in the [120] azimuth curves split streaks occur, whose spacing remains constant as the diffraction order increases; (ii) in the [130] azimuth the splitting is not resolved, which indicates that the point P (the crossover point in reciprocal space), whose position we cannot diffuse exactly, is very close to the [130] intersection; (iii) in the $[\bar{1}20]$ and $[\bar{1}30]$ azimuths (especially the former), the intersections are tangential to the corrugations, so the split-streak features are not present, and there is only an increase in the diffuse background intensity.

The corrugated sheet in reciprocal space could result from a zig-zag chain structure in real space, with a 4-Å repeat distance along the $[\bar{1}10]$ direction, to which the chain makes an angle of ~25°. We are unable to determine uniquely the point P, so we cannot be more specific about details of the chains at this stage. We will put this in the context of surface structural models in Sec. IV, after first discussing ARPES and core-level results.

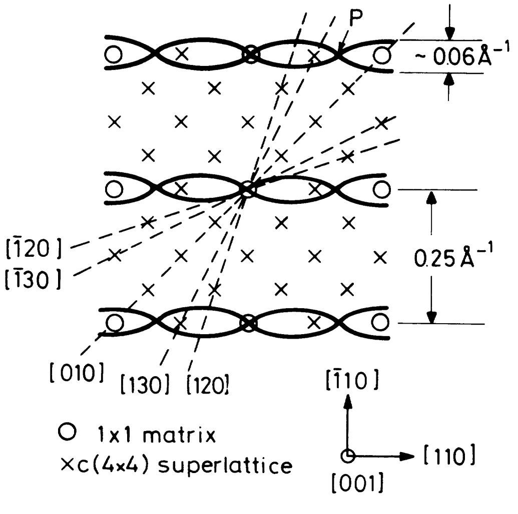

FIG. 2. Reciprocal-lattice section of the $c(4\times4)$ reconstruction. Solid lines represent sections through the reciprocal-lattice corrugated-sheet structure. Broken lines represent Ewald sphere projections (approximated by planes at the electron energies used) and show the intersections with the reciprocal lattice for the azimuths used. Distances in the figure are given in units of reciprocal space conventionally used in crystallography. They can, of course, be converted to wave-vector reciprocal space by multiplying by 2π.

B. Photoemission from the valence-band region

We have shown previously[7,11] that very marked differences can be observed between photoemission spectra obtained for the (2×4) and the $c(4\times4)$ reconstructions, and that surface-sensitive features can be identified by such a comparison. This is illustrated in Fig. 3, which shows angle-resolved energy distribution curves (AREDC's) at a number of photon energies for the $c(4\times4)$ structure (solid line curves) and the (2×4) structure (broken line curves). The spectra have been measured in the [010] azimuth at polar angles (θ_p), corresponding to a constant surface parallel wave vector $\vec{k}_{\parallel}$ equal to the $K_{1\times1}$ symmetry point of the unreconstructed (1×1) surface Brillouin zone (SBZ), and are plotted with the initial binding energy (E_b) referenced to the valence-band maximum (E_{VBM}). Since

$$k_{\parallel}=(2mE_k/\hbar^2)^{1/2}\sin\theta_p\ ,$$

where E_k is the electron kinetic energy, there is strictly only one initial energy (here $E_i\sim-1.0$ eV) for which $\vec{k}_{\parallel}$ is at the $K_{1\times1}$ point, but in the initial energy range between -3 eV and E_{VBM} and

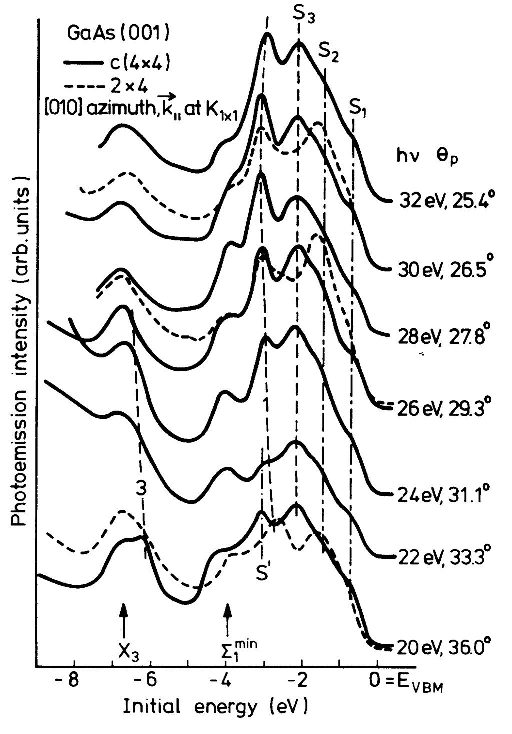

FIG. 3. AREDC's at a number of photon energies and polar angles, related to keep $\vec{k}_{\parallel}=K_{1\times1}$ for $E_i=-1$ eV, for the $c(4\times4)$ structure (solid lines) and the (2×4) structure (broken lines).

for photon energies in the range 20–32 eV, $\vec{k}_{\parallel}$ remains near $K_{1\times 1}$ to within 8% of the $K_{1\times 1}$ SBZ boundary momentum (1.111 Å^{-1}). Figure 3 shows that spectral differences between the two surface reconstructions are mainly found near E_{VBM} and a few eV below. Three features labeled S_1, S_2, and S_3 are observed for the $c(4\times 4)$ and not for the (2×4) structure, for which peaks and shoulders are seen at other energies. In addition to the dependence on the surface structure, S_1, S_2, and S_3 obey the criterion for surface states that they should not disperse with the momentum perpendicular to the surface, $\vec{k}_{\perp}$, for a constant $\vec{k}_{\parallel}$. It should further be noted that occupied valence bands only exist at the $K_{1\times 1}$ symmetry point for initial energies in the ranges -2.8 to -3.5 eV, -6.4 to -6.7 eV, and -10.4 to -10.7 eV,[8] so if surface umklapp processes can be neglected, all three states are true surface states since they do not overlap in energy with bulk states. They can only become surface resonances by surface umklapp through reciprocal surface lattice vectors.

At lower initial energies the AREDC's are dominated by transitions involving bulk states. The peaks near the energies of critical points (X_3, $\Sigma_1^{\min}$) are attributed to direct bulk interband transitions involving secondary cone emission and/or surface umklapp processes. It has been shown that a model of direct transitions from the valence bands to a quasi-free-electron final state describes bulk transitions well for both GaAs(110) (Ref. 20) and MBE-grown GaAs(001) (Ref. 8). The broken lines marked 1 and 3 in Fig. 3 represent the calculated dispersions derived from this model. The agreement with experiments is good for feature 3 in spectra from both (2×4) and $c(4\times 4)$ surfaces. Feature 1 agrees well for the (2×4) surface, but for the $c(4\times 4)$ surface there is almost no dispersion of the peak near -3.05 eV and a superposition of a surface resonance and a dispersing bulk peak cannot be ruled out. The initial energy positions of the surface states and/or resonances at the $K_{1\times 1}$ symmetry point are summarized in Table I for the (2×4) and the $c(4\times 4)$ reconstructions.

AREDC's have also been measured as a function of polar angle along the [110] and [$\bar{1}$10] azimuths, and the spectra are shown in Figs. 4(a) and 4(b). The feature S_1, indicated by a dashed line near the valence-band maximum, can be identified as a surface-state resonance using the procedure described above, whereas peaks and shoulders at lower initial energies (e.g., feature 3) are mainly due to emission from bulk valence bands. From angle-of-incidence dependence measurements the surface state S_1 can be identified to be mainly p_z-like, where z is the direction of the surface normal, i.e., these states are mainly dangling-bond-like.

Figure 5 shows the energy dispersion versus $\vec{k}_{\parallel}$ of the surface bands for the [110] and [$\bar{1}$10] azimuths, corresponding to the $\Gamma J_{1\times 1}$ and $\Gamma J'_{1\times 1}$ symmetry directions of the unreconstructed SBZ. Along the $\Gamma J_{1\times 1}$ direction the surface band has a rather large energy dispersion of about 0.65 eV, and its symmetry corresponds to the (1×1) SBZ. Along the $\Gamma J'_{1\times 1}$ direction the surface band displays a much smaller dispersion of about 0.20 eV, while the periodicity has doubled compared to the $\Gamma J_{1\times 1}$ periodicity. It is clear that the surface bands do not show the $c(4\times 4)$ symmetry of the surface structure as observed by the RHEED measurements. We will discuss further (in Sec. IV) the surface-state emission results and also refer to earlier results obtained for the (2×4) reconstruction.

To clarify certain aspects of the As core-level behavior, which we present in the next section (III C 1), we also briefly investigated the valence-band structure of As films deposited at room temperature on a GaAs substrate. The results are shown in Fig. 6 for a 2.5- and 7-monolayer (ML) As film together with the corresponding spectrum for the clean GaAs surface. We merely wish to indicate the close similarity of the 7-ML spectrum with those of Refs. 21–23 for amorphous As. In addition, the RHEED pattern from the deposit produced only diffuse halos.

C. As 3*d* and Ga 3*d* core levels

Surface chemical shifts have been resolved in the As 3*d* core levels for the $c(4\times 4)$ surface that yield

TABLE I. Initial energy position in eV of surface states and/or resonances for $\vec{k}_{\parallel}$ at the $K_{1\times 1}$ symmetry point.

(2×4)		$c(4\times 4)$			
S_2 (shoulder)	S_3 (peak)	S_1 (shoulder)	S_2 (shoulder)	S_3 (peak)	S'[a] (peak)
-0.85	-1.60	-0.70	-1.45	-2.15	-3.05

[a] Owing to overlap with bulk transitions the assignment of this peak as a surface resonance is tentative.

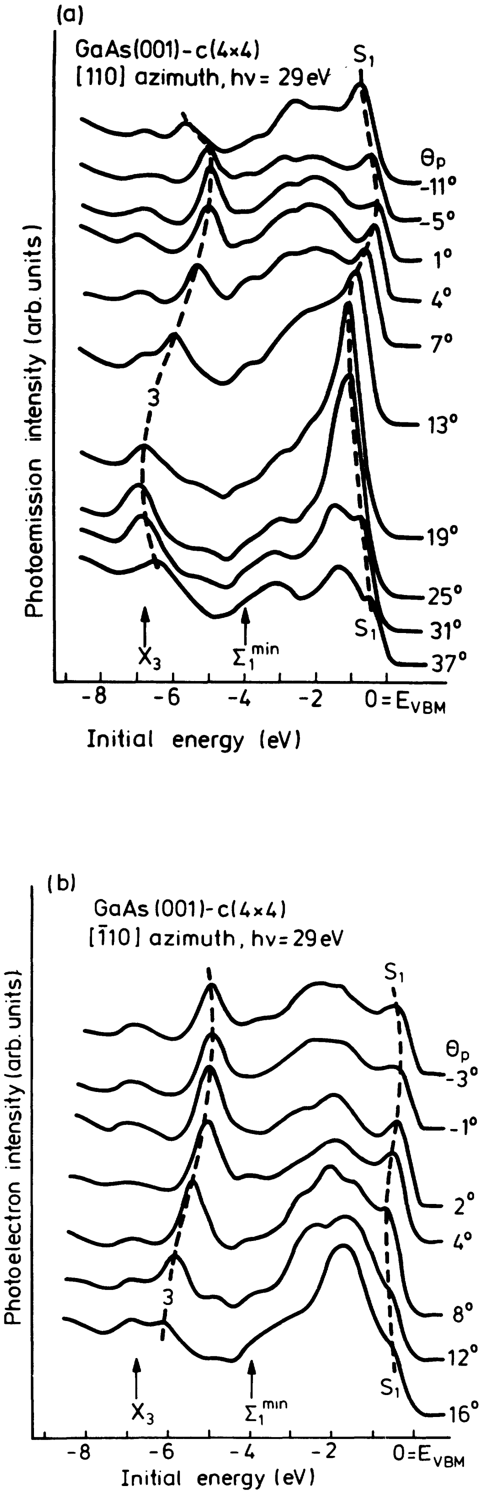

FIG. 4. AREDC's as a function of polar angle at $h\nu=29$ eV for the $c(4\times4)$ structure. (a) [110] azimuth; (b) $[\bar{1}10]$ azimuth.

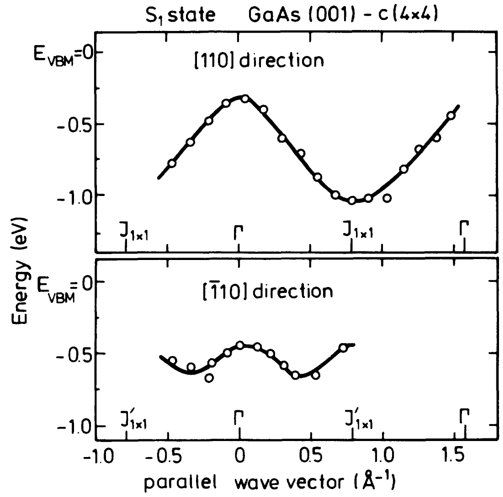

FIG. 5. Energy dispersion vs $\vec{k}_{\parallel}$ of the S_1 surface band for the [110] and $[\bar{1}10]$ azimuths, corresponding to the $\Gamma J_{1\times1}$ and $\Gamma J'_{1\times1}$ symmetry directions of the unreconstructed (1×1) SBZ.

information on the bonding of the surface As atoms (see Sec. III C 1). The surface As coverage may be estimated from an analysis of As 3*d* surface to bulk core-level intensity ratios, and also from As 3*d* to Ga 3*d* total intensity ratios (Sec. III C 2).

1. *Surface chemical shifts and surface bonding*

In Figs. 7(a) and 7(b) photoemission spectra of the As 3*d* core level taken at normal emission and $h\nu=72.7$ eV are shown for the GaAs(001)-(2×4) and $c(4\times4)$ reconstruction, respectively. Both sur-

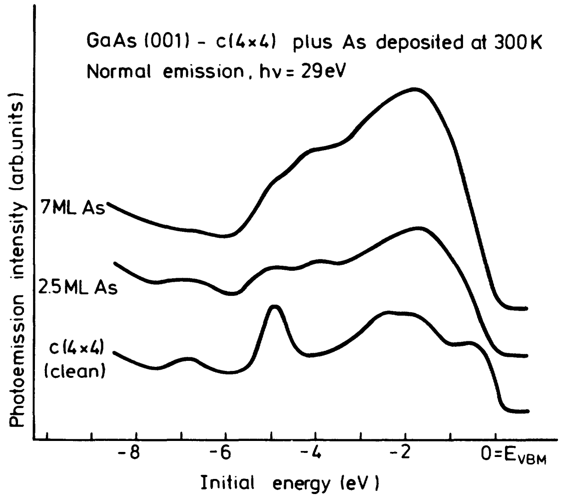

FIG. 6. Normal emission photoelectron-energy spectra at $h\nu=29$ eV for the clean $c(4\times4)$ structure and for a 2.5- and a 7-ML As overlayer.

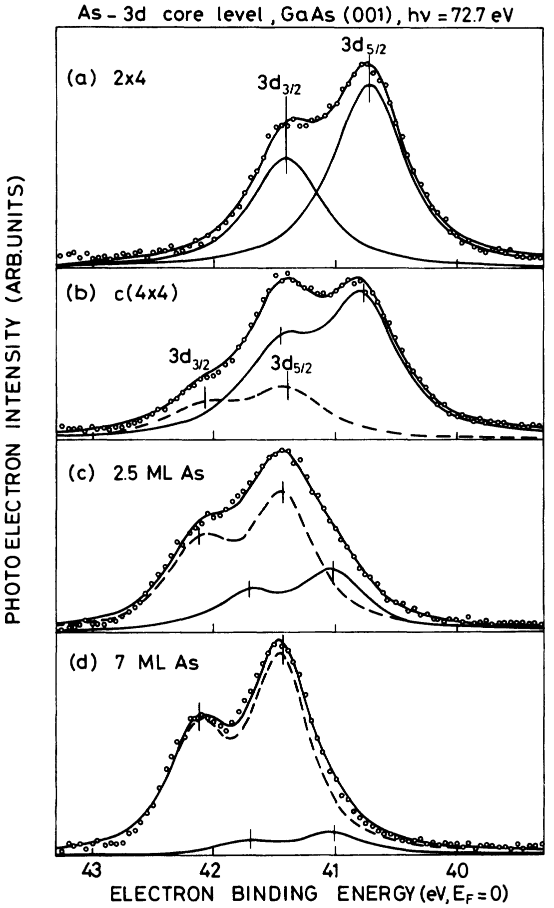

FIG. 7. As 3*d* core-level spectra taken at normal emission and $h\nu = 72.7$ eV. (a) (2×4) surface; (b) $c(4\times4)$ surface; (c) and (d) As films deposited on the $c(4\times4)$ surface.

faces were prepared using As_2 beams. For this photon energy the final energy of the photoelectrons (~ 32 eV) corresponds to a small escape depth (~ 5 Å, see Sec. III C 2) and therefore a high surface sensitivity. The binding energy is referred to the Fermi level E_F, which is located 0.4 ± 0.1 eV above the valence-band maximum.[24] A smooth, low background on which the original spectra were superimposed has been subtracted using a cubic spline fit. The energy positions indicated in Fig. 7(a) for the $3d_{3/2}$ and $3d_{5/2}$ levels were determined at low photon energy ($h\nu = 50$ eV), corresponding to a longer escape depth and a lower surface sensitivity. These binding energies when referenced to E_{VBM} are in good agreement with the bulk binding energies given by Eastman *et al.* for GaAs(110).[18]

The spectra were analyzed by a curve-fitting program using a Lorentzian line shape convoluted with a Gaussian resolution function having a full width at half maximum (FWHM) of 0.27 eV, which was the total instrumental resolution (monochromator plus analyzer). For the (2×4) surfaces only a single spin-orbit-split 3*d* doublet is required to fit the observed spectrum (solid line through the experimental points). The best-fit $3d_{3/2}$ and $3d_{5/2}$ levels are also shown in Fig. 7(a). The spectral width of each component is 0.59 eV (FWHM), the branching ratio $3d_{3/2}{:}3d_{5/2} = 0.60$, and the spin-orbit splitting is 0.68 eV. However, if we compare this spectrum with one measured at 50 eV for which the bulk contribution is dominant, we find that each 3*d* component of Fig. 7(a) is broadened 0.1–0.15 eV compared to the bulk levels. Considering now Fig. 7(b) for the $c(4\times4)$ surface, we note that there is a well-defined shoulder at the high-binding-energy side of the doublet and an apparent change of the branching ratio for the observed spectrum. This spectrum can be fitted, as shown in Fig. 7(b), if a shifted doublet (broken curve) is added to the unshifted doublet (lower solid curve). Both the shifted and unshifted doublets have the same spin-orbit splitting, branching ratio, and spectral width as determined for the (2×4) surface [Fig. 7(a)]. The binding-energy shift of the additional doublet compared to the unshifted is 0.62 eV, and the intensity ratio of the shifted to unshifted doublet is 0.365.

These results prove that the $c(4\times4)$ surface is chemically different from the (2×4) surface. We have also measured the As 3*d* line shape for the Ga-stable GaAs(001)-(4×6) surface and find it to be very similar to that of the (2×4) surface.[24] The line shapes of the Ga 3*d* levels are identical for the (2×4) and $c(4\times4)$ reconstructions.

The As 3*d* core levels for a 2.5- and 7-ML As film deposited on a GaAs(001) substrate at room temperature are shown in Figs. 7(c) and 7(d). The RHEED and valence-band data discussed in Sec. III B provide evidence that the As is amorphous. If we then compare Figs. 7(b) and 7(d), it is apparent that the binding energies of the two doublets indicated by the broken curves are identical. We note that the bonding in amorphous As is trigonal, and the similarities between the As 3*d* spectra for the $c(4\times4)$ reconstruction and amorphous As suggest similar bonding for the two structures. The lower solid curve in Fig. 7(d) represents the contribution from the GaAs substrate, which, due to band-bending effects, has been shifted by 0.3 eV toward higher binding energies compared to the (2×4) and $c(4\times4)$ bulk contributions.

2. *Core-level intensities and As coverage*

An estimate of the As coverage can, in principle, be made either from the surface to bulk As 3*d* intensity ratio or from the Ga to As core-level intensity ratio. We first derive an expression for the latter ratio, $R = I_{\mathrm{Ga}}/I_{\mathrm{As}}$. We assume a layer-by-layer model (alternating layers of Ga and As atoms) and use values for the escape depths appropriate to the different energies of the photoelectrons. We define

$$\alpha_i = a_0/[\lambda_i(E_i)4\cos\theta] ,$$

where the subscript i refers either to Ga or As, $a_0/4$ is the spacing between successive Ga and As planes, a_0 is the lattice parameter of GaAs, θ is the angle of emergence with respect to the surface normal (inside the solid), E_i is the final energy of the photoelectrons, and $\lambda_i(E_i)$ is the electron escape depth at E_i. θ is related to the polar angle θ_p of the detected electrons by

$$\theta = \sin^{-1}[\sin\theta_p/(1-V_0/E_k)]^{1/2} ,$$

where E_k is the kinetic energy and V_0 the inner potential [~ -14 eV for GaAs (Ref. 25)]. Then for GaAs(001) with alternating layers of Ga and As,

$$R = \beta\frac{1-y+y\exp(-\alpha_{\mathrm{Ga}})}{(1-y)\exp(-\alpha_{\mathrm{As}})+y} , \tag{1}$$

where y is the fractional surface occupancy of As and

$$\beta = \frac{1-\exp(-2\alpha_{\mathrm{As}})}{1-\exp(-2\alpha_{\mathrm{Ga}})}\frac{I^0_{\mathrm{Ga}}}{I^0_{\mathrm{As}}} . \tag{2}$$

I^0_{Ga} and I^0_{As} are the atomic photoelectron excitation ratios at $h\nu$ for the appropriate core levels of Ga and As, respectively. Hence we can express y in terms of R:

$$y = \frac{1-\dfrac{R}{\beta}\exp(-\alpha_{\mathrm{As}})}{\dfrac{R}{\beta}[1-\exp(-\alpha_{\mathrm{As}})]+[1-\exp(-\alpha_{\mathrm{Ga}})]} . \tag{3}$$

If values for the escape depths $\lambda_i(E_i)$ are known, or assumed, and $I^0_{\mathrm{Ga}}/I^0_{\mathrm{As}}$ is known, then the fractional coverage y can be found. The ratio $I^0_{\mathrm{Ga}}/I^0_{\mathrm{As}}$ can be obtained from measurements on the stoichiometric (110) surface using equations similar to Eqs. (1) and (2), but adapted to the (110) orientation.[9]

In any attempt to determine surface composition ratios from core-level intensity measurements, however, a number of critical assumptions and estimates must be made: (i) Any possible photoelectron diffraction effects are ignored, although Ludike and Ley have shown that they may be important for GaAs in some circumstances.[26] (ii) The photoelectron escape depth must be estimated. To obtain reasonable values of the escape depth we used the energy dependence of the data for $\lambda(E)$ for oxidized GaAs as measured by Pianetta *et al.*,[27] but adjusted the absolute scale to fit with measurements reported by Szajman *et al.*[28] for Ge, as shown in Fig. 8. The reason for adopting this procedure is that while the data of Pianetta *et al.* cover the appropriate energy range, they apply to oxides, whereas the Ge data are at higher energies than we used, but Ge and GaAs are very similar in many respects. It is clear, however, that this can only give an estimate for the escape depth, although in the absence of accurate values we believe it is the optimum approach.

With these assumptions and estimates, using intensity ratios for the $c(4\times4)$ and (2×4) structures at $h\nu=72.7$ eV and escape depths from Fig. 8 of $\lambda_{\mathrm{As}}(32\text{ eV})=5.4$ Å and $\lambda_{\mathrm{Ga}}(54\text{ eV})=4.8$ Å, we obtain for y the value $y(c(4\times4))\sim1.3y(2\times4)$. To estimate a value of $y(c(4\times4))$ we must attribute a value for $y(2\times4)$, and on the basis of our model for this surface,[7,11] we assume it to be close to unity. We note also that Bachrach *et al.*[9] estimate a surface As coverage of 0.89. Consequently, $y(c(4\times4))$ is in excess of unity, which in fact is not compatible with the formulation used. It indicates that the As coverage is in excess of a monolayer for the $c(4\times4)$ surface. Similarly, the data published by Bachrach *et al.*[9] at $h\nu=130$ eV with the appropriate escape depths from Fig. 8 yield $y(c(4\times4))=1.13$ and $y(2\times4)=0.99$. For y values above unity, implying the presence of more than one layer of As at the surface, we can reformulate the expressions for R,

$$R = \beta\frac{\{1+y'[\exp(-\alpha'_{\mathrm{Ga}})-1]\}\exp(-\alpha_{\mathrm{Ga}})}{1+y'[\exp(-\alpha'_{\mathrm{As}})-\exp(-2\alpha_{\mathrm{As}})]} , \tag{4}$$

from which one gets the overlayer concentration y':

$$y' = \frac{1-\dfrac{R}{\beta}\exp(\alpha_{\mathrm{Ga}})}{\dfrac{R}{\beta}\exp(\alpha_{\mathrm{Ga}})[\exp(-\alpha'_{\mathrm{As}})-\exp(-2\alpha_{\mathrm{As}})]+1-\exp(-\alpha'_{\mathrm{Ga}})} . \tag{5}$$

Here $\alpha'_i = d/[\lambda_i(E_i)\cos\theta]$, where d is the spacing between the As overlayer and the top As substrate layer. If we assume $\alpha'_i=\alpha_i$ and again $y(2\times4)\approx1$ we find $y'(c(4\times4))\sim0.4$ for our data and $y'(c(4\times4))=0.2$ for the data of Bachrach *et al.* There is probably an experimental uncertainty of

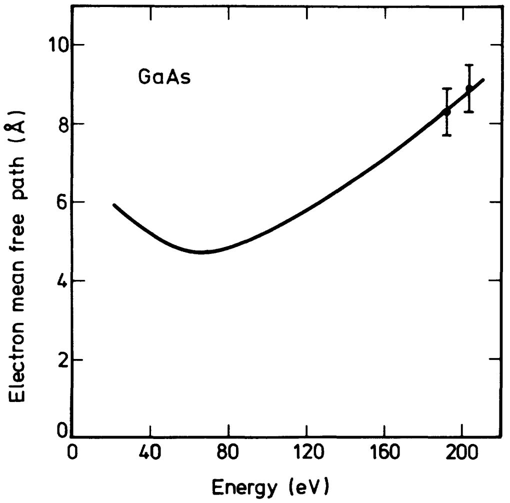

FIG. 8. Escape depth vs electron-energy curve derived from the data of Pianetta *et al.* (Ref. 27) for oxidized GaAs by fitting these to Ge data of Szajman *et al.* (Ref. 28) (shown as experimental points at 192 and 203 eV).

about 10% in the intensity ratios resulting from the measurements for the (110) reference surface. The point to emphasize here is that for both our Ga 3*d* to As 3*d* intensity ratio data and those of Bachrach *et al.*[9] the surface coverage of As is in excess of unity in a range from $\frac{1}{5}$ to $\frac{1}{2}$ (subject to the assumptions and estimates already enumerated).

There is other evidence from the preceding section dealing with the As 3*d* line-shape analysis that suggests an excess As overlayer. The intensity ratio ($\equiv Q$) of the shifted As 3*d* doublet to the unshifted doublet is 0.365. We can use this ratio to estimate the surface coverage of As if we make the additional assumption that the shifted doublet originates from the surface layer only. Then the overlayer concentration y' is given by

$$y' = \frac{Q}{1-\exp(-2\alpha_{\mathrm{As}})+Q[1-\exp(-\alpha'_{\mathrm{As}})]} . \tag{6}$$

Substitution of $Q=0.365$ and the appropriate escape depth for $h\nu=72.7$ eV and again assuming $\alpha'_{\mathrm{As}}=\alpha_{\mathrm{As}}$ give the value $y'(c(4\times4))\simeq0.75$. The difference between this value and the other two estimates is not surprising in view of the simple nature of our model and the complete neglect of diffraction effects. In the former two cases the photoelectrons from Ga and As have substantially different energies, and diffraction effects could easily influence the relative intensities, whereas in the latter case the photoelectron energies for the shifted and unshifted As 3*d* level only differ by 0.6 eV and any differential diffraction effect will be small.

So, without specifying the actual fractional coverage of excess As, the evidence is consistent with an excess layer. This conclusion can only be altered by taking considerably smaller and probably unreasonable values of escape depth, and these would also tend to give values of As occupancy of less than 0.5 for the (2×4) surface, which is inconsistent with other measurements.

Finally, we believe that the excess coverage required to give the $c(4\times4)$ structure is not a fixed amount, but can vary considerably, so the particular coverages referred to above are typical rather than absolute. Our reason for this belief comes principally from the RHEED observation that the same surface symmetry is maintained over a considerable range of As exposures, the observation of which is supported by the Auger-electron spectroscopy results of Massies *et al.*[29]

IV. DISCUSSION

We will first consider what features must be incorporated into any model of the $c(4\times4)$ surface to maintain consistency with the experimental data presented here and with previously published results. The principal characteristic, derived from analysis of the core-level line shapes and intensities (Sec. III C), is that the $c(4\times4)$ structure has a surface As population greater than 1 ML; i.e., there is more As than would be present on the ideal As-terminated (001) surface. This $c(4\times4)$ symmetry can also be maintained over a rather wide range of excess As coverage y', where $0.2\leq y'\leq0.75$ is a reasonable estimate on the basis of the photoelectron escape depth model described in Sec. III C. It should be noted that Massies *et al.*[29] also suggested that a wide As coverage range exists for the $c(4\times4)$ structure. The analysis of the As 3*d* line shape in spectra from (2×4) and $c(4\times4)$ surfaces in comparison with that obtained from an amorphous As overlayer leads to the conclusion that the excess As is bonded only to As atoms in the surface, not to Ga. In agreement with this, Ga 3*d* core-level spectra show identical line shapes for (2×4) and $c(4\times4)$ surfaces.

If we now consider the surface crystallography as determined by RHEED, two essential components must be included in the model. It must obviously display $c(4\times4)$ symmetry, but in addition it should incorporate a periodic zig-zag chain arrangement, with a repeat distance of 4 Å in the $[\bar{1}10]$ direction, to which the chain makes an angle of 25°.

The photoemission results in the valence-band region show that the structures of the $c(4\times4)$ and (2×4) surfaces are distinctly different. This is apparent, for example, from the surface states at the $K_{1\times1}$ symmetry point as shown in Fig. 3. For the (2×4) surface we have previously observed a nearly dispersionless band at about -3 eV, which is in close agreement with a calculated band associated with an asymmetric As-As dimer band and which we believe to be the essential characteristic of the (2×4) surface.[11] This band is not observed for the $c(4\times4)$ surface, implying the absence of the type of dimer bond involved in the (2×4) reconstruction. In addition, we observe a surface band near the valence-band maximum that is derived from dangling-bond-like states but does not reflect the $c(4\times4)$ symmetry. There is only onefold periodicity along the [110] azimuth, while it is doubled along the $[\bar{1}10]$, corresponding effectively to a (2×1) "unit cell" for the dangling-bond states, probably reflecting the substrate. This is merely an indication of the extent of orbital overlap from these bonds in the two directions. The dispersion of the band along the [110] direction (about 0.65 eV) is of the order to be expected from a next-nearest-neighbor interaction of dangling bonds via backbonds.[30] For the $[\bar{1}10]$ direction it is considerably smaller, indicating less interaction between the dangling bonds in this direction.

The only detailed model for the $c(4\times4)$ structure that has so far been proposed is due to Chadi *et al.*,[15] and was derived solely from theoretical considerations. On the basis of energy minimization calculations they suggested that two distinct types of As-As dimers are involved. The first is the asymmetric or noncoplanar dimer, which corresponds to the dimerization scheme that we proposed for the (2×4) surface.[11] The second type of dimer is symmetric, i.e., coplanar. The theoretical model of the $c(4\times4)$ reconstruction has equal amounts of these two dimer types in the surface layer.

It would, however, appear to have several weaknesses in relation to the experimental evidence we have presented above. Firstly, is assumes only monolayer As coverage, whereas the experimental observations are consistent with a coverage of more than one monolayer, and furthermore it does not allow for surface As atoms bonded only to other As atoms. Finally, for the $c(4\times4)$ structure we do not observe an asymmetric dimer bond band, while this band is very apparent with the (2×4) surface. We must conclude, therefore, that the model proposed by Chadi *et al.* does not seem appropriate.

To maintain consistency with the experimental evidence we believe that models for the $c(4\times4)$ structure should be derived from an As-terminated surface on which additional As is chemisorbed, but they should also include features representative of amorphous As, in keeping with the observed As $3d$ core-level behavior. In terms of As—As bonding, therefore, it would ideally be trigonal, with a bond length of 2.49 Å and a bond angle of 98.2°.[31]

In Figs. 9(a) and 9(b) we present possible models for the $c(4\times4)$ structure that correspond to 25% and 50% extra As coverage, respectively. Both models are based on chemisorbed As trigonally bonded to surface As atoms. We have assumed that As—As bond lengths are the same as in amorphous As and have allowed the bond angle to distort. The proposed structures can be achieved with a reasonably small distortion ($\sim9°$) to give a bond angle for the surface structure of $\sim107°$. In Fig. 9(b) we have indicated the outlines (by arrows) of a zig-zag chain structure, which has a repeat distance of 4 Å along the $[\bar{1}10]$ direction. The atoms involved are not coplanar, so the RHEED pattern corresponding to the corrugations would be complex, as observed. We note that the angles involved would not be too different from the 25° suggested in Sec. III A. Figures 9(a) and 9(b) should not be considered as separate models for the $c(4\times4)$ surface, but rather we suggest that combinations of both structures can coexist as the amount of adsorbed As changes; i.e., we emphasize that the $c(4\times4)$ structure does not correspond to a specific As coverage. This explains why the symmetry of the diffraction pattern does not change over a substantial range of exposures to As, although of course the intensity of the diffracted beams is not necessarily constant. Note that from electron-counting arguments it follows that the proposed surface models are consistent with the surface being semiconducting, as found experimentally. The absence of the dimer bond band in the valence-band photoemission of the $c(4\times4)$ structure can simply be explained by the change from As dimer to trigonal bonding in going from the (2×4) to the $c(4\times4)$ reconstruction.

Finally, we consider surface core-level energy shifts, which in general for semiconductors require a complex interpretation in terms of changes in the intra-atomic potential, in the interionic Madelung potential and in the screening of the final-state hole.[32] However, the specific case of different binding energies between elemental As and As atoms bonded in GaAs can be understood in terms of ionic charges. If we consider the 7-ML deposited As film, then from the RHEED evidence of a diffuse ring pattern and the similarity of the valence-band spectra with those reported for amorphous As,[21–23] we may conclude that the film is amorphous As, as we indicated in Sec. III C 1. Neighboring As atoms are therefore covalently bonded. For GaAs, however, the bonding is partly ionic,[33] with some of the bonding charge between Ga and As displaced towards the As atom. This lowers the As core-level

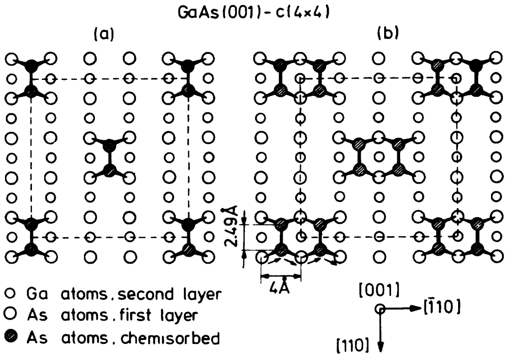

FIG. 9. Possible models for the $c(4\times4)$ surface based on a trigonally bonded excess As layer. (a) an additional 25% As coverage; (b) an additional 50% As coverage.

binding energy with respect to that in amorphous As, in agreement with the observed shift of 0.62 eV. This can be converted into a charge in valence charge using a simple electrostatic model proposed by Brennan *et al.*[34] in which it is assumed that the effect of charge transfer on the core-level binding energy is the same as the effect of core-electron charge transfer on the valence band. For the valence band the effect of one less core electron is the same as that of one more proton in the nucleus, a good approximation of the core-level shift resulting from the loss of one electron from the valence band is the change in hybrid energy between $Z-1$, Z, and $Z+1$, i.e., Ge, As, and Se in this case. From Harrison's data,[35] the value is about 1.9 eV/electron, and so a core-level shift of 0.62 eV implies a charge transfer δq of $\sim$0.33 electron/atom in bulk GaAs, well within the range $0.3<\delta q<0.4$ electron/atom quoted by Davenport *et al.*[32] Thus the larger binding energy found for the $c(4\times4)$ surface, which is the same as that for amorphous As, suggests that the excess As is bonded to surface As rather than Ga atoms, which is borne out by the absence of any shifts in the Ga $3d$ binding energy between (2×4) and $c(4\times4)$ surfaces. This behavior is again consistent with our proposed models.

In summary, we have presented evidence that in the $c(4\times4)$ structure the As coverage is in excess of 1 ML and that the reconstruction is overlayer derived, based on trigonally bonded chemisorbed As. The models proposed are consistent with experimental observations from RHEED, ARPES, and surface-sensitive core-level photoemission. They also explain how the reconstruction symmetry can be maintained with a variable As coverage.

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[1] A. Y. Cho and J. R. Arthur, Prog. Solid State Chem. 10, 157 (1975).
[2] P. Drathen, W. Ranke, and K. Jacobi, Surf. Sci. 77, L162 (1978).
[3] A. Y. Cho, J. Appl. Phys. 47, 2841 (1976).
[4] J. H. Neave and B. A. Joyce, J. Cryst. Growth 44, 387 (1978).
[5] P. J. Dobson, J. H. Neave, and B. A. Joyce, Surf. Sci. 119, L339 (1982).
[6] J. Massies, P. Devoldere, and N. T. Linh, J. Vac. Sci. Technol. 16, 1244 (1979).
[7] P. K. Larsen, J. H. Neave, and B. A. Joyce, J. Phys. C 14, 167 (1981).
[8] P. K. Larsen, J. F. van der Veen, A. Mazur, J. Pollmann, and B. H. Verbeek, Solid State Commun. 40, 459 (1981).
[9] R. Z. Bachrach, R. S. Bauer, P. Chiaradia, and G. V. Hansson, J. Vac. Sci. Technol. 18, 797 (1981); 19, 335 (1981).
[10] P. K. Larsen and J. F. van der Veen, J. Phys. C 15, L431 (1982).
[11] P. K. Larsen, J. F. van der Veen, A. Mazur, J. Pollmann, J. H. Neave, and B. A. Joyce, Phys. Rev. B 26, 3222 (1982).
[12] J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. B 14, 1623 (1976).
[13] J. Pollmann and S. T. Pantelides, Phys. Rev. B 18, 5524 (1978).
[14] I. Ivanov, A. Mazur, and J. Pollmann, Surf. Sci. 92, 365 (1980).
[15] D. J. Chadi, C. Tanner, and J. Ihm, Surf. Sci. 120, L425 (1982).
[16] P. K. Larsen, W. A. M. van Bers, J. M. Bizau, F. Wuilleumier, S. Krummacher, V. Schmidt, and D. Ederer, Nucl. Instrum. Methods 195, 245 (1982).
[17] J. H. Neave, P. Blood and B. A. Joyce, Appl. Phys. Lett. 36, 311 (1980).
[18] D. E. Eastman, T.-C. Chiang, P. Heiman, and F. J. Himpsel, Phys. Rev. Lett. 45, 656 (1980).
[19] P. Delescluse and A. Masson, Surf. Sci. 100, 423 (1980).
[20] T.-C. Chiang, J. A. Knapp, M. Aono, and D. E. Eastman, Phys. Rev. B 21, 3513 (1980).

[21] L. Ley, R. A. Pollak, S. P. Kowalczyk, F. R. McFeely, and D. A. Shirley, Phys. Rev. B 8, 641 (1973).

[22] C. Y. Su, I. Lindau, P. R. Skeath, I. Hino, and W. E. Spicer, Surf. Sci. 118, 257 (1982).

[23] N. J. Shevchik and S. G. Bishop, Phys. Rev. B 12, 1567 (1975).

[24] J. F. van der Veen, L. Smit, P. K. Larsen, and J. H. Neave, in Proceedings of the 16th Conference on the Physics of Semiconductors, Montpellier, France, 1982 [Physica B (in press)].

[25] P. Mark, G. Cisneros, M. Bonny, A. Kahn, C. B. Duke, A. Paton, and A. R. Lubinsky, J. Vac. Sci. Technol. 14, 910 (1977).

[26] R. Ludeke and L. Ley, J. Vac. Sci. Technol. 16, 1300 (1979).

[27] P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. B 18, 2792 (1978).

[28] Y. Szajman, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, J. Electron Spectrosc. Relat. Phenon. 14, 41 (1978).

[29] J. Massies, P. Etienne, F. Dezaly, and N. T. Linh, Surf. Sci. 99, 121 (1980).

[30] J. Pollmann (private communication).

[31] G. N. Greaves and E. A. Davies, Philos. Mag. 29, 1201 (1974).

[32] J. W. Davenport, R. E. Watson, M. L. Perlman, and T. K. Sham, Solid State Commun. 40, 999 (1981).

[33] W. A. Harrison, Phys. Rev. B 10, 767 (1974).

[34] S. Brennan, J. Stöhr, R. Jaeger, and J. E. Rowe, Phys. Rev. Lett. 45, 1414 (1980).

[35] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980), p. 50.

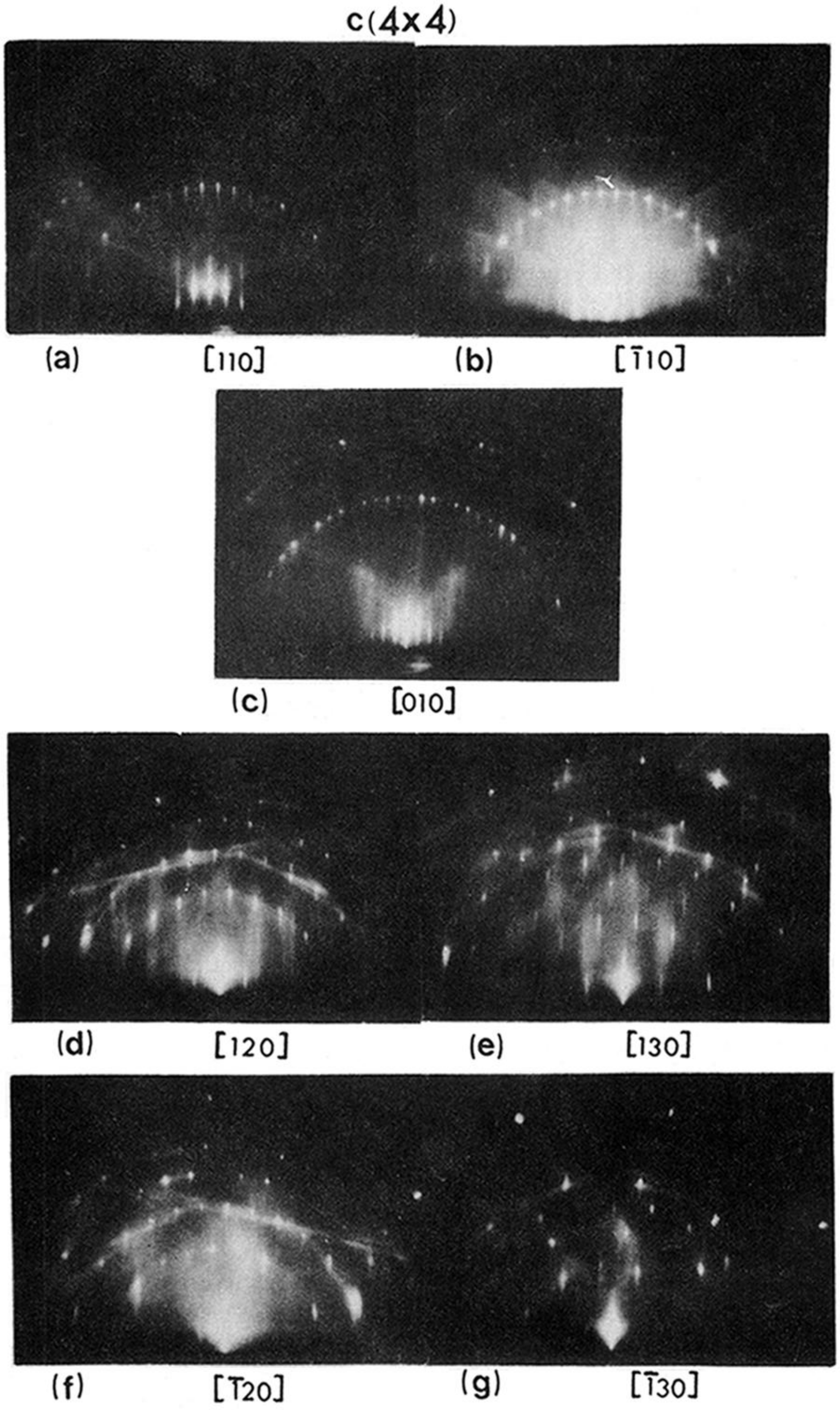

FIG. 1. RHEED patterns for various azimuths of GaAs(001)-$c(4\times4)$.