Reflectance Anisotropy of GaAs(100): Theory and Experiment

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The reflectance anisotropy has been calculated by microscopic tight-binding theory for various configurations of the As-rich GaAs(100) $c(4 \times 4)$ and (2×4) reconstructions, based on precise atomic coordinates from *ab initio* total-energy minimization. The comparison to experimental reflectance anisotropy in combination with scanning tunneling microscopy and low energy electron diffraction allows one to identify precise correlations between structural units and optical features. Clear indications are obtained for the intermediate steps in the surface reconstruction transformation. [S0031-9007(98)06681-2]

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Optical spectroscopy has become an important tool of surface analysis in the last years, due to its high sensitivity and *in situ* applicability [1]. In particular, reflectance anisotropy spectroscopy (RAS) is increasingly used for monitoring the growth of epitaxial structures in molecular beam epitaxy (MBE) or in metal organic vapor pressure epitaxy (MOVPE) [1–4]. However, theoretical understanding is needed in order to fully exploit its potential.

Among the technologically important (100) surfaces of III–V semiconductors, the most intensively studied "prototype" is GaAs(100). A variety of different reconstructions, dependent on surface stoichiometry, exist; the three main reconstructions are the As-rich $c(4 \times 4)$, the As-rich $(2 \times 4)/c(2 \times 8)$, and the Ga-rich $(4 \times 2)/c(8 \times 2)$ phases [2–6]. Several structural models of the As-rich phases are discussed in the literature [7–9] (see Fig. 3): At high As coverage the $c(4 \times 4)$ phase should consist of three top As dimers bonded to the next complete As monolayer. Annealing up to around 400 °C leads to the $(2 \times 4)/c(2 \times 8)$ phase. Total energy calculations [7–9] predict two different stable (2×4) geometries depending on the preparation conditions: the so-called $\beta 2$ and the α structure. The $\beta 2$, containing two top As dimers and one As dimer in the exposed third layer, accounts for the $(2 \times 4)/c(2 \times 8)$ phase. The so-called α structure is characterized by Ga dimers in the second layer besides the two top As dimers.

The local atomic structure of the surface has often been claimed to play a key role in determining the surface optical anisotropy [1–5]. Hence, using a reliable theoretical description it should be possible to relate the optical response to the atomic surface structure. At present, few examples of good agreement between experiments and calculations of the optical response based on the one-electron band structure approximation, employing semiempirical tight-binding [10–12] as well as *ab initio* plane-wave expansions [13], are available. For GaAs(100), however, theoretical results are rather unsatisfactory [14,15], and recently it was hypothesized that RAS line shapes in many cases may have little to do with the atomic structure of the surface, but are rather determined by surface-induced changes of excitonic and local-field effects on bulk transitions [16,17] which are not included in the above mentioned calculations.

In this work, we demonstrate that calculations based on the one electron band structure approximation indeed yield a good description of experimental data, provided that a realistic atomic structure is assumed. For this purpose STM and RAS experiments are combined with structure determination via total-energy minimization and tight-binding calculation of optical properties. Our findings demonstrate the existence of precise correlations between atomic structure and optical properties. They cannot be overwhelmed by the approximately structure-independent surface-exciton and local-field effects.

We determine the precise surface geometry from density-functional theory within the local-density approximation, using a molecular-dynamics approach [18]. We consider a periodic slab of eight or seven atomic (100) layers within a (2×4) and (4×4) supercell, respectively. Single-particle orbitals are expanded into plane waves up to an energy cutoff of 15 and 10 Ryd for (2×4) and (4×4) reconstructions, respectively. The special **k** points used correspond to 64 points in the full (1×1) two-dimensional Brillouin zone (2DBZ). The minimum energy configurations have nearly symmetric As dimers (bond lengths of 2.50–2.57 Å) and an almost planar bonding of the threefold coordinated second-layer Ga atoms. For the α structure the Ga dimer length is 2.51 Å. A detailed account of these calculations is given elsewhere [8,9].

We calculate the optical properties by the sp^3s^* tight-binding approach, which has proven successful for a number of homopolar surfaces [10–12]. To separate the contributions of the two opposite surfaces, which yield different optical properties, a linear cutoff function was used in calculating the optical matrix elements. Checks for GaAs(110), where the two surfaces of the slab are equivalent, demonstrate that the linear cutoff does not introduce any spurious optical anisotropy. We found that 20 layers are necessary to avoid the artificial interaction between the two sides of the slab. To avoid a possible spurious optical asymmetry due to the 2DBZ **k**-point summation, a $p(4 \times 4)$ supercell (containing around 300 atoms) with 4 special **k**-points in its irreducible part [equivalent to 256 **k**-points in the (1×1) 2DBZ] has been used.

As-capped homoepitaxial GaAs(100) layers grown by MBE were used in the experiments. After transfer to the UHV chamber, clean GaAs(100) surfaces were prepared by thermal desorption of the As cap [6]. The aim of our experiments is to correlate the stages seen by LEED and RAS during subsequent annealing steps in UHV with structural changes displayed by STM due to the gradual As surface depletion. RAS spectra acquired for subsequent annealing steps, starting with the well-known $c(4 \times 4)$ surface structure, are shown in Fig. 1. The $c(4 \times 4)$ and $(2 \times 4)/c(2 \times 8)$ structures produced within this cycle reveal the expected line shapes, as reported previously [2,3,5]. Here we focus on the evolution of the RAS spectra from the $c(2 \times 4)$ to the $(2 \times 4)/c(2 \times 8)$, correlated with the gradual As surface depletion. The STM image (Fig. 2) shows how the transition is accomplished through the formation of intermediate, local defect-structures. In regions where the topmost As dimers of the regular three-dimer $c(4 \times 4)$ structure are missing, STM clearly indicates the formation of a local $(2 \times n)$ structure, due to dimerization of the As exposed in the second layer. During transition from $c(4 \times 4)$ to (2×4), LEED reveals a (1×1) pattern due to the lack of long range order, while a gradual change of the surface reflectance anisotropy (Fig. 1) is attributed to the superposition of the optical response of the different, locally coexistent structure phases [$c(4 \times 4)$, $(2 \times n)$, (2×4)].

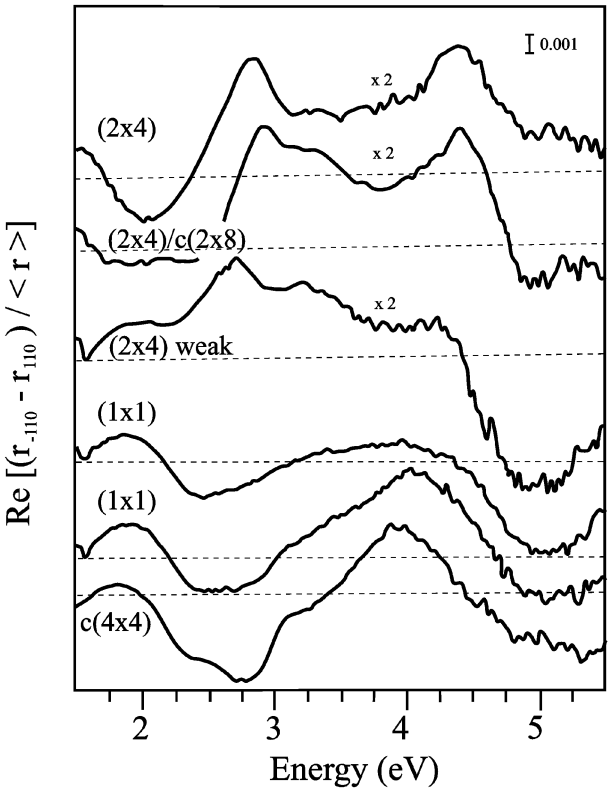

FIG. 1. Experimental RAS spectra for As-rich surfaces recorded *in situ* after decapping and subsequent annealing of undoped GaAs(100) (spectra taken at room temperature). Annealing temperature increases from bottom to top. The dashed lines denote the zero level for each spectrum. The corresponding LEED patterns are indicated for each RAS curve.

In Fig. 3 we present the calculated RAS spectra together with schematics of the corresponding atomic structures for the As-rich 3-dimer $c(4 \times 4)$, the $\beta 2(2 \times 4)$ and $\alpha(2 \times 4)$ structures, and, moreover, for a multilayer relaxed (2×1) dimer model structure, to account for the local $(2 \times n)$ structure observed by STM. The (2×1) structure produces a negative RAS feature at 2.4 eV, opposite to that observed for the $(2 \times 4)/c(2 \times 8)$ phase (Fig. 1), although the orientation of the As surface dimers is the same. Therefore, in contrast to previous suggestions [14], the (2×1) structure cannot be used as a simplified model for the real (2×4) phase for understanding the surface optical anisotropy. This result means that the surface dimers themselves are not necessarily the dominant source of the optical anisotropy, as has often been assumed so far. In contrast, the precise structure of the uppermost few atomic layers has to be considered.

The RAS spectra calculated for the $c(4 \times 4)$ and $\beta 2(2 \times 4)$ reconstructions [the latter has to be compared to the $(2 \times 4)/c(2 \times 8)$ experimental curve] show an excellent overall agreement with experiment. They

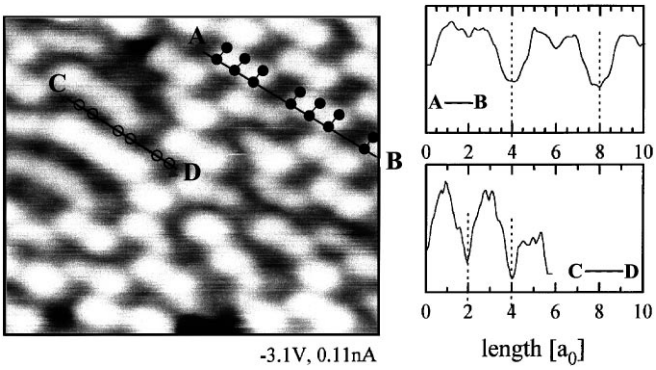

FIG. 2. STM image of a GaAs(100) surface at the transition between $c(4 \times 4)$ and (2×4) phases. Most parts of the image correspond to an As-deficient structure, the upper right corner displays a regular $c(4 \times 4)$ reconstructed region. In the regular region each bright block consists of three As dimers, followed by one missing dimer. The As surface dimers are partially marked by black dots, the line scan (*A*-*B*) shows the fourfold periodicity. In the As-deficient regions longer sequences of As dimers appear, however separated by three or more lattice distances n, exposing As of the second layer in between. The resulting structure corresponds to a $(2 \times n)$ phase, since the exposed As of the second layer dimerizes (partially marked by open dots). The twofold periodicity in the second layer is shown in the line scan (*C*-*D*).

are characterized by two main features, a low-energy feature around 2.8 eV (slightly below the E_1 critical energy) which reverses its sign from $c(4 \times 4)$ to (2×4), and a high-energy one between 4.2 and 4.7 eV which remains essentially unaffected. The low energy feature is dominantly related to the presence of the As surface dimers, consistent with its sign change during the $c(4 \times 4)$-(2×4) transition. The common positive feature at higher energies around 4.2–4.7 eV is mainly due to the modification of bulk wave functions induced by the crystal termination. This feature is essentially diminished on disordered surfaces, as revealed by additional calculations (not shown here) after insertion of surface defects. Thus, this feature is correlated with the perfection of the long range order at the surface rather than with the structural unit [17]. In case of local coexisting different structure phases, the surface derived optical transitions (approximately up to 3.5 eV) consist of a mixture of the different contributions due to the local sensitivity of the optical response, while the bulk derived features at higher energies are well defined only when LEED indicates a good long range ordering.

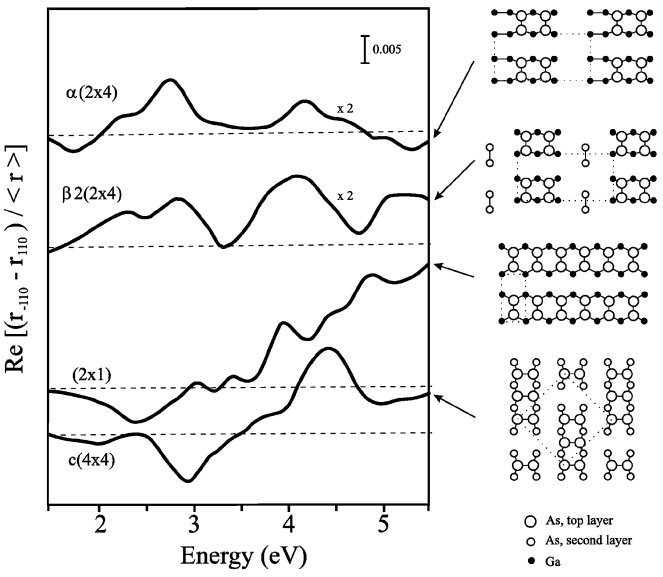

FIG. 3. Calculated RAS spectra for the $c(4 \times 4)$, (2×1), $\beta 2(2 \times 4)$ [corresponding to the $c(2 \times 8)$ structure in the decapping experiment], and $\alpha(2 \times 4)$ structures. The atomic structures used in the calculations are schematically shown on the right hand side. The dashed lines denote the zero level for each spectrum.

The calculations reproduce very well the amplitude of the experimental RAS spectra in the case of the $(2 \times 4)/c(2 \times 8)$ structure, while for the $c(4 \times 4)$ phase the experimental RA is approximately 2 times smaller. We attribute this to the presence of quite a number of defects at the real $c(4 \times 4)$ surface (see STM image in Fig. 2) which reduces and broadens the optical features.

The experimental curve for the $c(4 \times 4)$ reconstruction shows an additional positive feature around 1.8 eV and a negative shoulder around 2.4 eV, which both become most pronounced for the transitional "(1×1)" structures (see Fig. 1) and are absent in the calculated RA. Recalling the finding of the negative RAS feature in the calculated spectrum of the (2×1) structure and the STM observation of the $(2 \times n)$-like local dimerization (Fig. 2), one can interpret the experimental shoulder at 2.4 eV as a signature of a local dimerization of second layer As. The positive feature at 1.8 eV can be modeled by calculating the RAS for a metastable $c(4 \times 4)$ structure with two top As dimers instead of three [9], which may occur locally during gradual As depletion. Thus for the $c(4 \times 4)$ and transitional "(1×1)" phases the experimental peaks below 2 eV and the shoulder at 2.4 eV are due to the removal of the top As atoms, exposing the partially dimerized As in the second layer.

During further As depletion a pronounced minimum develops at 2 eV in RAS while LEED changes from $(2 \times 4)/c(2 \times 8)$ to (2×4) (Fig. 1, top curve). The RAS signal indicates that this (2×4) phase is not equivalent to a $\beta 2(2 \times 4)$ structure anymore but corresponds to the $\alpha(2 \times 4)$ model: In the calculated RAS a negative feature around 1.8 eV is found for the $\alpha(2 \times 4)$ structure, characteristic for the presence of second layer Ga dimers. To our knowledge, this is the first confirmation of the $\alpha(2 \times 4)$ phase which has been predicted by theory [7–9].

Tight-binding calculations of the optical properties of GaAs(100) have been previously carried out in Ref. [14] for the As-rich (2×4) phase. The agreement to experiment, however, was rather poor since the structure models

used there were markedly different from the meanwhile accepted $\beta 2(2 \times 4)$ model [19]. More recently, first-principles calculations for the α, $\beta 2(2 \times 4)$, and $c(4 \times 4)$ structures [15] were carried out. For computational difficulties, however, an unrealistically thin slab (four layers) and a rather limited kinetic-energy cutoff of only 7 Ry were used. As a consequence, poor agreement with experiment was obtained. We get, on the contrary, good agreement in line shape and amplitude with experimental data for all the different structure phases, whose presence has been confirmed by STM measurements. These findings show that accurate geometries and rather thick slabs are needed to calculate surface optical properties in a reliable way. Without these two ingredients, the calculated optical properties may differ *qualitatively* from the measured ones.

In conclusion, the present results clearly demonstrate that the RAS line shape does in fact depend sensitively on the atomic structure and the stoichiometry of the surface, in such a way that the presence of a given structural unit can be inferred from the presence of its (calculated) features in the (measured) RAS spectrum. However, a simple correlation of the optical anisotropy just with the surface dimers does not give an adequate description. In contrast, converged calculations of the surface optical properties based on precise atomic geometries are required. The good agreement obtained demonstrates also that excitonic or local-field effects have no major influence.

Finally, we suggest that the underlying approach should be applied to other semiconductor surfaces as well. Theoretical links between structural units and spectral features may then help to decide between conflicting structure proposals for a surface reconstruction.

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Note added in proof.—During the process of publication of this Letter an article (Eryiğit and Herman [20]) appeared, reporting calculations of surface optical properties for (2×4) GaAs(100) reconstructions, where the anisotropy of the H-covered back surface was not subtracted. Some calculations of ours, not shown here, demonstrate that H-covered GaAs(100) surfaces have optical anisotropies of the same order, or even larger, than clean surfaces. Hence the good agreement with experiments claimed in this reference may be fortuitous.

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[1] *Epioptics: Linear and Nonlinear Optical Spectroscopy of Surfaces and Interfaces*, edited by J. McGilp *et al.* (Springer-Verlag, Berlin, 1995), and references therein.

[2] I. Kamiya, D. E. Aspnes, L. T. Florez, and J. P. Harbison, Phys. Rev. B **46**, 15 894 (1992).

[3] W. Richter, Philos. Trans. R. Soc. London A **344**, 453 (1993).

[4] W. Richter and J.-T. Zettler, Appl. Surf. Sci. **100/101**, 465 (1996).

[5] D. Pahlke, M. Arens, N. Esser, and W. Richter, Surf. Sci. **352–354**, 66 (1996).

[6] U. Resch-Esser, N. Esser, D. T. Wang, M. Kuball, J. Zegenhagen, B. O. Fimland, M. Cardona, and W. Richter, Surf. Sci. **352–354**, 71 (1996).

[7] J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993); G. P. Srivastava, and S. J. Jenkins, Phys. Rev. B. **53**, 12 589 (1996).

[8] W. G. Schmidt and F. Bechstedt, Surf. Sci. Lett. **360**, L473 (1996); Phys. Rev. B **54**, 16 742 (1996).

[9] N. Moll, A. Kley, E. Pehlke, and M. Scheffler, Phys. Rev. B **54**, 8844 (1996).

[10] C. Noguez, C. Beitia, W. Preyss, A. I. Shkrebtii, M. Roy, Y. Borensztein, and R. Del Sole, Phys. Rev. Lett. **76**, 4923 (1996).

[11] P. V. Santos, B. Koopmans, N. Esser, W. G. Schmidt, and F. Bechstedt, Phys. Rev. Lett. **77**, 759 (1996).

[12] A. Selloni, P. Marsella, and R. Del Sole, Phys. Rev. B **33**, 8885 (1986)

[13] L. Kipp, D. K. Biegelsen, J. E. Northrup, L.-E. Swartz, and R. D. Bringans, Phys. Rev. Lett. **76**, 2810 (1996).

[14] S. F. Ren and Y.-C. Chang, Phys. Rev. B **44**, 13 573 (1991); Y.-C. Chang and D. Aspnes, Phys. Rev. B **41**, 12 002 (1990).

[15] S. J. Morris, J. M. Bass, and C. C. Matthai, Phys. Rev. B **52**, 16 739 (1995); J. M. Bass and C. C. Matthai, J. Vac. Sci. Technol. B **14**, 3075 (1996).

[16] U. Rossow, L. Mantese, and D. E. Aspnes, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors, Berlin 1996*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 831.

[17] K. Uwai and N. Kobayashi, Phys. Rev. Lett. **78**, 959 (1997).

[18] R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994).

[19] A recent x-ray diffraction experiment has confirmed the occurrence of the $\beta 2$ structure [Y. Garreau, M. Sauvage-Simkin, N. Jedrecy, R. Pinchaux, and M. B. Veron, Phys. Rev. B **54**, 17 638 (1996)].

[20] R. Eryiğit and P. Herman, Phys. Rev. B **56**, 9263 (1997).