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Geometric structure and optical properties of the GaAs(001)-$c(4\times4)$ surface

C. Hogan,* E. Placidi, and R. Del Sole
Dipartimento di Fisica, Università di Roma "Tor Vergata," and Istituto Nazionale per la Fisica della Materia,
Via della Ricerca Scientifica 1, 00133 Roma, Italy

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We consider the electronic structure and optical properties for several geometries of the GaAs(001)-$c(4\times4)$ surface using first-principles calculations. We find strong evidence that the best agreement with photoemission and reflectance anisotropy spectroscopy experiments carried out on surfaces prepared under As_4 flux is obtained for a structure containing three Ga–As dimers per unit cell. The standard As–As dimer model yields similar, but distinguishable results, while an asymmetric dimer model is found to yield completely incompatible surface spectra.

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The GaAs(001) surface is of prime importance in the fabrication of electronic and optoelectronic devices based on molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOVCD) technologies.[1] Although the surface exhibits a wide variety of stoichiometries, epitaxial growth is optimal under As-rich conditions, which lead to (2×4) and $c(4\times4)$ reconstructions. The latter is particularly important for growth where relatively low temperatures are required, such as in the self-organized growth of InAs quantum dot systems[2] and in magnetic dilute semiconductors.[3] Nevertheless, it is astounding that so much controversy persists over its basic atomic structure. The widely accepted model of the GaAs(001)-$c(4\times4)$ reconstruction is the symmetric dimer structure consisting of three As dimers adsorbed on a complete layer of As atoms [Fig. 1(a)]. The existence of this structure was proposed on the basis of grazing-incidence x-ray diffraction experiments[4] and STM images[5] and was further supported by first-principles calculations of the total energy[6] and reflectance anisotropy.[7] However, many unresolved issues remained that weaken this consensus, leading several authors to suggest alternative surface structures.[8,9]

For instance, two independent low-energy electron diffraction (LEED) studies[10,11] proposed slight modifications to the three-dimer model, in the form of asymmetrical, variable-length dimers and considerable in-plane twisting [Fig. 1(c)]. Much research has focused on structures with a different stoichiometry. Based on reflectance anisotropy spectroscopy (RAS) and scanning tunneling microscopy (STM) measurements, Ohtake and co-workers[8,12] proposed the existence of a new phase having a mixed dimer (heterodimer) structure as illustrated in Fig. 1(b), existing independently of the symmetric dimer phase with preparation conditions determining which phase is actually obtained. The mixed dimer phase, illustrated in Fig. 1(b), is found[12] to be kinetically stable when the (2×4) is cooled in As_4 fluxes. Under As_2 flux, however,[12] it is metastable and appears just for a narrow range of temperatures below the transition occurring at 510–490 °C; below this temperature the symmetric phase appears instead, albeit mixed with the heterodimer phase, and becomes "pure" as the temperature decreases below 340 °C.[13] Growth of the symmetric dimer structure under As_2 flux had previously been predicted in first-principles chemisorption studies.[14]

On the other hand, *ab initio* simulations demonstrated that the mixed dimer phase is less stable than both (2×4) and $c(4\times4)$ symmetric phases across the full range of Ga chemical potential.[12] More recent works[15,16] which considered the thermodynamic properties of a wide range of GaAs(001) stoichiometries also found the mixed dimer structure to be unfavored, consistent with its observed metastable character under As_2 flux. Nonetheless, the observation in STM of a mixed dimer structure under As_4 flux remains largely unexplained. In fact, the apparently inconsistent behavior of the $c(4\times4)$ surface may be due to dynamical factors.[12]

Although the $(2\times4)\rightarrow c(4\times4)$ transition under As flux can be monitored with STM, a most convincing display of how the surface composition evolves was provided by Ohtake *et al.*[12] through the use of reflectance anisotropy spectroscopy (RAS). Many of the conclusions made about

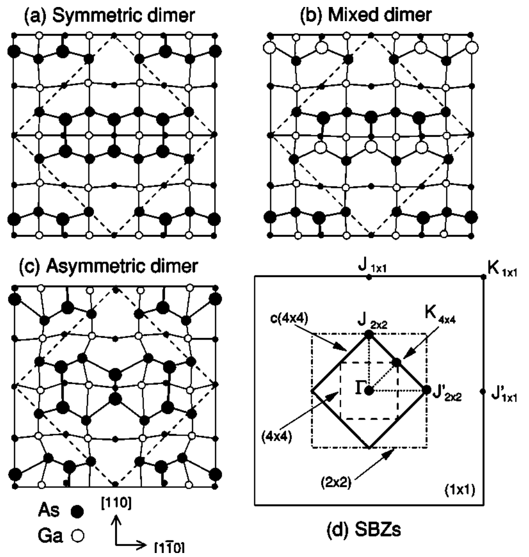

FIG. 1. Schematic representations of the GaAs(001)(4×4) surface: (a) symmetric dimer model; (b) mixed dimer model; (c) asymmetric dimer model. In (d) the $c(4\times4)$ surface Brillouin zone is shown referred to the primitive (1×1), (2×2), and (4×4) zones.

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the $c(4\times4)$ structure are based on phenomenological studies of RAS spectra changes during surface preparation. However, correct interpretation of experimental spectra can generally only be provided via first-principles calculations. In this paper we study in detail the role of RAS in elucidating the structure of the $c(4\times4)$ reconstruction of GaAs(001). We give strong evidence that the conclusions of Ohtake and coworkers are correct, and we provide the link between the observed spectra and the geometric structure. As there seems to be a distinct lack of theoretical study of the electronic structure of the $c(4\times4)$ surface and its surface states, we also consider the band structures of these phases and compare them with experiment.

Calculations of the structure, wave functions, and optical properties were carried out within density-functional theory in the local density approximation (DFT-LDA), using ABINIT (Ref. 17) and a molecular-dynamics Car-Parrinello code. Plane waves (18 Ry cutoff) and norm-conserving pseudopotentials were used throughout, and relativistic effects were not considered. The GaAs(001) surfaces were modeled using a repeated slab scheme, with supercells consisting of 11 layers of GaAs and about 10 Å of vacuum. The theoretical value for the lattice constant at 18 Ry, $a_0=5.58$ Å, was used. The surfaces were allowed to relax until all forces were less than 40 meV/Å. The back two layers, as well as a terminating layer of fractionally charged H, were kept fixed to their ideal positions. We include a dipole correction in the vacuum to remove the spurious macroscopic field induced by the boundary conditions. A single optimized **k** point was used for the ground-state calculations.

The relative change of surface reflectivities, $\Delta R/R = (R_{[1\bar{1}0]}-R_{[110]})/R$, where R_x denotes the reflectivity for light polarized along the x direction, is obtained from the slab dielectric tensor,[18] computed using 18 **k** points in the irreducible part of the $c(4\times4)$ surface Brillouin zone (BZ). This yields spectral peak positions converged to a precision better than 100 meV. Finally, to enable meaningful comparison of energies with experiment, we apply a rigid scissors shift[19] of 0.5 eV to the unoccupied states; this is an optimized value chosen to account for self-energy and excitonic shifts in energy.

TABLE I. Dimer lengths for the $c(4\times4)$ surface models. Values in parentheses are those of Ohtake *et al.* (Ref. 8).

	Mixed	Symmetric	Asymmetric
Inner dimer (Å)	2.44 (2.46)	2.49	1.93
Outer dimers (Å)	2.46 (2.48)	2.52	3.20

Schematic diagrams of the reconstructions are shown in Fig. 1. Initial coordinates for the mixed dimer and asymmetric dimer surfaces were obtained, after normalizing to the theoretical lattice constant, from the DFT calculations of Ohtake *et al.*[8] and the LEED fitted data of Romanyuk *et al.*,[11] respectively.

Considering first the asymmetric dimer structure, we found that it is higher in energy than the symmetric model by 1.79 eV/(1×1) cell. This is a prohibitively large value, corresponding to initial forces exceeding 1 eV/Å. On relaxation, the skewed dimers quickly return to the symmetric configuration of Fig. 1(a). We therefore conclude the asymmetric dimer structure to be physically unrealistic. In particular, we note that the outer dimer length, indicated in Table I, is extremely large in comparison with the As–As distance in As bulk (2.49 Å, Ref. 20) or in the As_4 molecule (2.44 Å, Ref. 10), and begins to approach the As–As distance of the fully unreconstructed surface (3.95 Å). Stretching the outer dimers by 0.7 Å greatly weakens the bridging σ orbitals (the interaction falls approximately as the square of the dimer length) and increases the overlap between the dimer atoms in adjacent cells, yielding a metallic ground state. The stability of the mixed dimer model relative to the symmetric one has been studied by other authors.[12,15]

In Fig. 2 we present calculated surface band structures within DFT-LDA of the symmetric and mixed dimer structures. On top of the projected bulk band structure, we indicate with (large) dots those states in the slab calculation that are identified as being (strongly) localized at the surface. To avoid use of nonstandard nomenclature, points lying on the $c(4\times4)$ BZ edge are named according to the corresponding points of the primitive (2×2) and (4×4) Brillouin zones (Fig. 1).

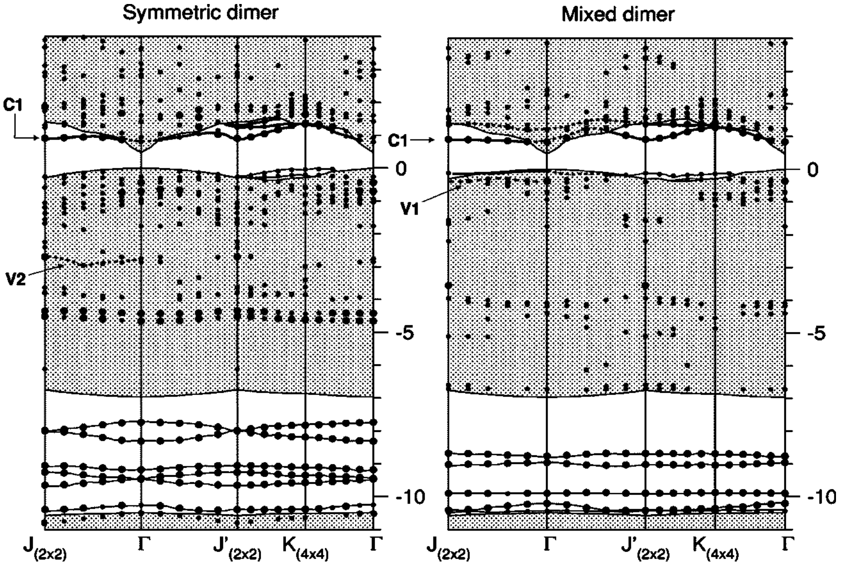

FIG. 2. DFT-LDA band structure of the GaAs(001)-$c(4\times4)$ surface, for the symmetric and mixed dimer models. (Large) dots indicate states (strongly) localized at the surface. The shaded region marks the (computed) projected bulk band structure.

TABLE II. Energetic positions (in eV) of the main electronic surface features identified in Fig. 2, compared with experimental values of possible surface states identified in ultraviolet photoemission spectroscopy (UPS). Energies are shown for the Γ point, unless stated otherwise, and are relative to the valence-band maximum (VBM).

	Mixed dimer	Symmetric dimer	Experiment
A	−0.3	−0.4	−0.5,[a] 0.0,[b] −0.4[c]
B	−1.8	−1.8	−2.0,[a] −1.3,[b] −1.7[c] ($K_{1\times1}$)
C	−4.2	−4.5	
D	−6.8		−6.0,[a] −6.5,[b] −6.8[c]
E		−7.8, −8.3	

[a] Strasser *et al.* (Ref. 21).

[b] Olde *et al.* (Ref. 22). Position of VBM may be slightly shifted (Ref. 22).

[c] Larsen *et al.* (Ref. 23). State D assumed to derive from bulk.

Overall, the band structures appear quite similar. Both feature a distinctive unoccupied surface state ($C1$) lying just below the conduction band edge which becomes resonant with the bulk band structure around the Γ point. The state shows almost no dispersion along the Γ–J direction, i.e., perpendicular to the dimer rows, and a stronger dispersion (of about 0.4 eV) in the Γ–J' and J'–K directions. A few filled and empty surface states are visible inside the bulk gap around the J' and K points in both cases, as are a cluster of bands inside the bulk-forbidden region below −7.5 eV.

In Table II we have summarized the main features of the surface band structures and compared them with experimental values obtained from photoemission experiments, which are reported to about −8.5 eV. In both reconstructions, a strongly localized surface state (A) is observed at about −0.4 eV around the Γ point. At least for the mixed dimer case, this state (indicated as V1) appears to be weakly dispersive along the Γ–J and Γ–J' directions. This would appear to coincide with the surface state identified in experiment between 0.0 and −0.5 eV. Weaker states appearing around −1.8 eV may correspond to that experimentally detected between −1.3 and −2.0 eV, although, as noted by Strasser *et al.*,[21] states at this energy are strongly resonant with the bulk and hence difficult to resolve in the calculation.

Several clear differences, however, allow us to distinguish between the two band structures: (i) The strong surface-localized bands appearing at −4.5 eV and around −8.0 eV in the symmetric dimer case are not observed in experiments (the mixed dimer model shows only a weak feature around −4.2 eV); and (ii) in contrast to the symmetric model, a weakly dispersive band (D) occurs for the mixed dimer model near the valence-band minimum at −6.8 eV, close to experimental features noted between −6.0 and −6.8 eV. Although the latter feature has been attributed to the X_3 bulk critical point,[22,23] it was not reproduced within theoretical UPS spectra assuming the symmetric dimer phase structure,[21] and a superposition of bulk and surface contributions cannot be excluded. These observations lead us to identify the $c(4\times4)$ surfaces observed by the authors of Refs. 21–23 with the mixed dimer phase, as we would expect on comparing their experimental conditions with those of Ohtake *et al.* (Ref. 12).

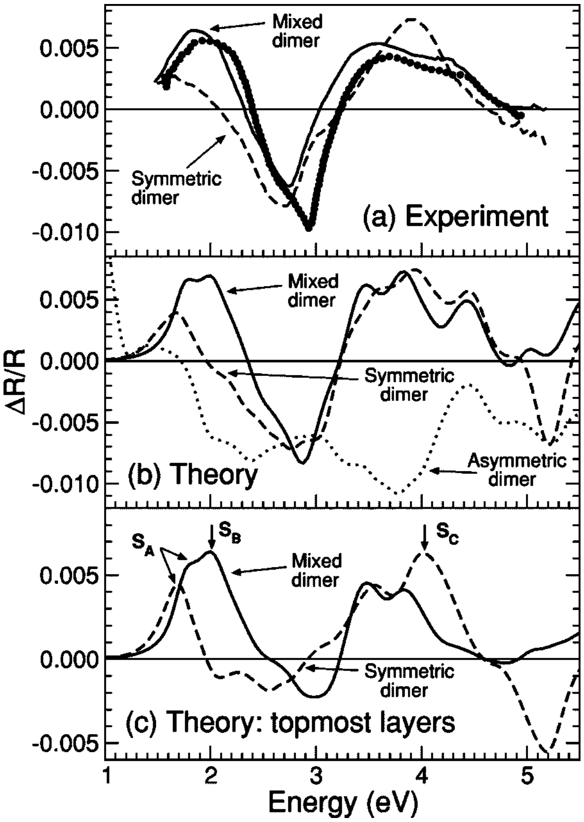

FIG. 3. RAS spectra of the GaAs(001)−$c(4\times4)$ surface. (a) Lines: experimental data from Ohtake *et al.* (Ref. 12); points: data of Ref. 24, for a surface prepared with As_4 flux. (b) Theoretical results. (c) Spectra from topmost layers only.

In Fig. 3(b) we present *ab initio* calculated RAS spectra for the three surface models depicted in Fig. 1. These are plotted with the experimental spectra, shown in (a), for the two proposed phases of GaAs(001)-$c(4\times4)$. The agreement between experiment and theory is generally very good. Specifically, we note that (i) the mixed dimer model shows in the theory a double-peaked feature at 1.8 eV and 2.0 eV, corresponding to the broad experimental peak at 1.9 eV, whereas only a single weaker feature is present in the symmetric dimer spectra; (ii) the negative structure around the bulk E_1 critical point at 2.9 eV is narrower and sharper for the mixed dimer spectra; and (iii) the peak (plateau) nature exhibited by the experimental symmetric (mixed) dimer phase around 4 eV is generally recovered in the theoretical spectra of the corresponding models. In contrast, the spectrum corresponding to the asymmetric dimer model is dramatically different from the experiment.

Comparison of our mixed dimer calculation with the carefully obtained data of Arciprete *et al.*[24] reveals an agreement that is remarkably good below 3.5 eV, *even in the intensity*. The agreement worsens at higher energy where the calculation becomes more sensitive to the convergence with respect to the number of slab layers and **k** points. The excellent agreement obtained at the level of DFT-LDA points to a strong cancellation of errors, as noted by Schmidt *et al.*,[25] or even to an absence of higher order effects (e.g., excitonic) on the line shape.

A clear difference between the experimental spectra of the mixed and symmetric dimer phases is the peak at 4 eV occurring only for the latter structure. The calculated spectra shown in Fig. 3(b) confirm this finding, although the experimental line shapes are not fully reproduced. The feature is more distinct when we extract that part of the signal coming from the top three atomic layers, as shown in Fig. 3(c). According to our analysis of the wave-function localization, this structure (S_C) is related to transitions, again along Γ–J, between low-energy dimer bonding orbitals existing only on the symmetric dimer structure ($V2$), and the chainlike $C1$ state. The strong surface localization and anisotropy of this transition enables it to be used as a signature of the $c(4\times4)$ symmetric dimer phase.

In conclusion, we have presented a theoretical study of the electronic and optical properties of GaAs(001)-$c(4\times4)$. In particular we have offered strong evidence that, of the various models proposed in recent years, the mixed dimer model provides the best fit to photoemission and RAS experiments for measurements performed on surfaces obtained by cooling the sample under As_4 flux. For $c(4\times4)$ surfaces obtained with As_2 cooling and As decapping procedures,[7] the symmetric dimer model seems to be suitable. Conversely, we have shown that asymmetric dimer models, derived from fitting to LEED data,[10,11] are not able to explain such experimental results. This work is a step towards a better comprehension of the geometry and electronic structure of both $c(4\times4)$ models and should help to solve many controversial interpretations present in the literature.

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*Electronic address: cdhogan@roma2.infn.it

[1] J. Faist, F. Capasso, D. L. Sivco, C. Sirtori, A. L. Hutchinson, and A. Y. Cho, Science **264**, 553 (1994).

[2] F. Patella, M. Fanfoni, F. Arciprete, S. Nufris, E. Placidi, and A. Balzarotti, Appl. Phys. Lett. **78**, 320 (2001).

[3] H. Ohno, Science **281**, 951 (1998).

[4] M. Sauvage-Simkin, R. Pinchaux, J. Massies, P. Claverie, N. Jedrecy, J. Bonnet, and I. K. Robinson, Phys. Rev. Lett. **62**, 563 (1989).

[5] A. R. Avery, D. M. Holmes, J. Sudijono, T. S. Jones, and B. A. Joyce, Surf. Sci. **323**, 91 (1995).

[6] J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993).

[7] W. G. Schmidt, F. Bechstedt, K. Fleischer, C. Cobet, N. Esser, W. Richter, J. Bernholc, and G. Onida, Phys. Status Solidi A **188**, 1401 (2001).

[8] A. Ohtake, J. Nakamura, S. Tsukamoto, N. Koguchi, and A. Natori, Phys. Rev. Lett. **89**, 206102 (2002).

[9] Z. M. Wang and G. J. Salamo, Phys. Rev. B **67**, 125324 (2003).

[10] A. Nagashima, M. Tazima, A. Nishimura, Y. Takagi, and J. Yoshino, Surf. Sci. **493**, 227 (2001).

[11] O. Romanyuk, P. Jiříček, M. Cukr, and I. Bartoš, Surf. Sci. **566–568**, 89 (2004).

[12] A. Ohtake, P. Kocán, J. Nakamura, A. Natori, and N. Koguchi, Phys. Rev. Lett. **92**, 236105 (2004).

[13] Transition temperatures and ranges may depend, of course, on the As flux intensity.

[14] C. G. Morgan, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **82**, 4886 (1993).

[15] E. Penev, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **93**, 146102 (2004).

[16] T. Ito, K. Tsutsumida, K. Nakamura, Y. Kangawa, K. Shiraishi, A. Taguchi, and H. Kageshima, Appl. Surf. Sci. **237**, 194 (2004).

[17] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (http://www.abinit.org).

[18] F. Manghi, R. Del Sole, A. Selloni, and E. Molinari, Phys. Rev. B **41**, 9935 (1990).

[19] R. Del Sole and R. Girlanda, Phys. Rev. B **48**, 11 789 (1993).

[20] Values taken from http://www.webelements.com

[21] T. Strasser, C. Solterbeck, W. Schattke, I. Bartoš, M. Cukr, and P. Jiříček, Phys. Rev. B **63**, 085309 (2001).

[22] J. Olde, G. Mante, H.-P. Barnscheidt, L. Kipp, J.-C. Kuhr, R. Manzke, M. Skibowski, J. Henk, and W. Schattke, Phys. Rev. B **41**, 9958 (1990).

[23] P. K. Larsen, J. H. Neave, J. F. van der Veen, P. J. Dobson, and B. A. Joyce, Phys. Rev. B **27**, 4966 (1983).

[24] F. Arciprete, C. Goletti, E. Placidi, P. Chiaradia, M. Fanfoni, F. Patella, C. Hogan, and A. Balzarotti, Phys. Rev. B **68**, 125328 (2003).

[25] W. G. Schmidt, F. Bechstedt, W. Lu, and J. Bernholc, Phys. Rev. B **66**, 085334 (2002).