Structure of GaAs(100)-c(8 × 2)-Ga

J. Cerdá, F. J. Palomares,* and F. Soria

Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, c/ Serrano 144, E-28006 Madrid, Spain

The crystallography of the GaAs(100)-c(8 × 2)-Ga surface, prepared by simultaneous cycles of Ar ion bombardment and annealing at 825 K, has been determined by a low energy electron diffraction I-V analysis. A model consisting of three adjacent dimers and a dimer vacancy yielded the best fit. The main feature of the corresponding structure is the presence of two different types of Ga dimers at the surface. The dimer in the middle is fully dimerized ($d_{Ga-Ga} = 2.13$ Å), while the dimerization for the Ga atoms in both outer dimers is much more subtle ($d_{Ga-Ga} = 3.45$ Å).

The characterization of semiconductor surfaces and, in particular, the polar surfaces of III-V compounds is of fundamental importance due to their implications in semiconductor devices. Despite the fact that from the pioneering work of Cho [1] on the polar GaAs(100) surface almost twenty years have passed, most of the crystallographic information relative to the multiple reconstructions that this surface exhibits still remains unknown [2]. While some partial structural studies by reflection high energy electron diffraction (RHEED) have been performed on the As rich $c(4 \times 4)$ and $p(2 \times 4)/c(2 \times 8)$ reconstructions [3], this is especially true for the Ga rich $p(4 \times 6)$ and $c(8 \times 2)$ ones, on which there is, to our knowledge, no complete structural analysis attempted to date. In the present contribution we address this point and perform a full crystallographic determination of the GaAs(100)-$c(8 \times 2)$-Ga reconstruction by means of a low energy electron diffraction (LEED) I-V curve analysis [4].

Based upon previous experimental [5–14] and theoretical [15,16] studies, there exist three different models that might accommodate the $c(8 \times 2)$ reconstruction and can be regarded as plausible. They are pictured in Fig. 1 and labeled A, B, and C. Models A and B consist of (4×2) subunits formed by three and two adjacent dimers separated by one and two missing dimers, respectively. They correspond to the β and $\beta2$ phases studied in Ref. [15], where it was concluded that the latter showed a greater stability. Both models were later challenged by Skala *et al.,* who proposed model C to interpret their scanning tunneling microscopy (STM) images [13]. Surprisingly, this model assumes an As terminated surface, where the As top atoms dimerize forming chains along the [110] direction, and the exposed second layer Ga atoms are also dimerized along the [110]. Very recently, Xue *et al.* gave a different interpretation to similar STM images strongly supporting model B [14].

For our analysis, we have used as substrates n-type GaAs(100) Si-doped (10^{18} cm^{-3}) on-axis wafers. The cleaning of the samples and the experimental system have been described in detail before [17]. It is well known that GaAs(100) samples bombarded with Ar^{+} at 600 eV and room temperature reach a steady state surface composition

of 0.56 Ga monolayer (ML) and 0.44 As ML [18]. If the treatment is done simultaneously with annealing cycles (SIBA) at about 800 K, an incompletely ordered $c(8 \times 2)$ structure is formed, while if the annealing is done at 825 K, a well-ordered $c(8 \times 2)$ structure is attained. I-V curves were recorded at normal incidence at about 140 K and at a base pressure of 5×10^{-10} Torr with a commercial AUTOLEED system. At this pressure, the $c(8 \times 2)$ phase remains clean for over a day. All the spectra could be well reproduced after renewed surface preparation. The LEED pattern consistently showed pmm symmetry (mirror planes [110] and [$\bar{1}$10] in Fig. 1). The final experimental data set consisted of 17 symmetry-inequivalent beams spanning a
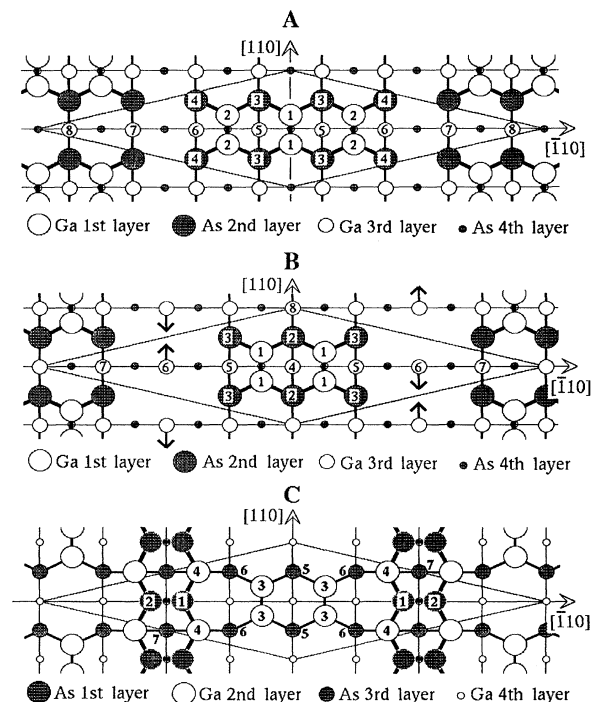

FIG. 1. The three models studied in this work for the GaAs(100)-$c(8 \times 2)$-Ga. Atoms indicated by the same number are symmetry equivalent. The elongated rhombus defines the superlattice unit cell.

total energy range of 2053 eV (1027 and 1026 eV for the integral- and fractional-order spectra, respectively).

The lack of previous crystallographic determinations on this surface, together with the complexity of the models depicted in Fig. 1 (which can involve up to 20 structural parameters), clearly reveal the huge hyperspace volume that needs to be explored in order to perform a reliable structural determination. To this end, the analysis of the experimental I-V curves was carried out in three stages, each involving different levels of sophistication in the multiple scattering formalism. First, NP searches within the linear LEED (LLEED) scheme [19] were performed over a wide-range grid, including parameters in the first two or three layers (typically, around ten parameters were simultaneously varied). Only symmetry preserving structures were considered throughout [20]. Several thousand geometries were chosen as references, and the subsequent amplitude mixing [19] yielded over 10×10^6 trial structures for each model. An extended beam set neglect (BSN) approach [21] was employed to evaluate the reference amplitudes, whereby all beams of order $(2n + 1, m/2)$ were neglected from both the plane wave basis and the experimental data. The scattering between the remaining beam sets was then treated exactly [4]. Real and reciprocal space-symmetrized codes [4,22] were used, and the calculations involved seven phase shifts per element. The agreement was quantified by an average R_{AV} of the Pendry R factor R_P [23], and that defined by Moritz, R_{DE} [24]. While the former pays special attention to peak and minima positions, the latter simply compares relative intensities. In order to filter errors in the choice of nonstructural parameters, R_P minima were also retained after these searches, regardless of the corresponding R_{DE} value. The precision of the BSN approach is mirrored by values of $R_{AV} < 0.07$ when compared with full-dynamical calculations, while the BSN + LLEED scheme yielded slightly higher values ($R_{AV} \approx 0.10$). The local R-factor minima encountered in this first stage were further checked by reduced dynamical NP searches (still within the BSN approach), comprising 500 to 1000 geometries. These minima were then explored by Tensor LEED (TLEED) [25]. To this end, a modified version of the automated TLEED package codes (ATLEED) [26] was used, in which layer doubling was incorporated for the reference structure calculation [27] and the Levenberg-Marquardt algorithm (LM) [28] was used to locate the minimum, fitting simultaneously beam intensities and their corresponding Y functions [27]. All parameters included in the first three layers were optimized.

Model A resulted in the best agreement with $R_{AV} = 0.50$ ($R_P = 0.48$ and $R_{DE} = 0.51$), while models B and C yielded significantly worse R-factor minima ($R_{AV} = 0.58$ and $R_{AV} = 0.56$, respectively). In Fig. 2 we sketch the geometry corresponding to the global minimum. The R-factor variance around this minimum [23] results in a value of $\Delta R_{AV} = 0.06$, which conclusively excludes the latter models as plausible. Therefore, the central point of this Letter is the presence of a three Ga dimer structure with one dimer vacancy for our $c(8 \times 2)$-Ga reconstruction prepared by SIBA, corresponding to a surface coverage of $\theta(\text{Ga}) = 0.75$ and $\theta(\text{As}) = 1.0$. Quantitative Auger electron spectroscopy [7] and photoelectron spectroscopy (PES) [11] estimates are in accordance with this coverage. This result is also consistent with HREELS data [5] and work-function measurements [9,11], provided a transfer of charge is assumed from the Ga atoms to the As4 atoms in the second layer [11]. Medium energy ion scattering data [12] corroborate this model too, although some As/Ga intermixing might be expected at the As4 sites. We have not studied this case, however, as it would require nonsymmetric structures, and the effect on the spectra should be minor.

At a final stage, a refinement of the optimized structure found by TLEED was carried out via LM minimizations, this time using a full-dynamical formalism (that is, including all the experimental data set as well as the complete plane wave basis). Also, Debye temperatures were optimized within the same scheme. The R-factor minimum was hardly modified, attaining a value of $R_{AV} = 0.49$ ($R_P = 0.50$ and $R_{DE} = 0.48$) for the geometry depicted in Fig. 2. Error bars for parameters normal to the surface are estimated around ± 0.1 Å, while for lateral displacements the accuracy is ± 0.2 Å for the first two layers, and ± 0.3 Å for the third. Thus displacements from their bulk positions for the third layer Ga atoms cannot be assured. The nonstructural parameters for the optimal model are $V_0 = 6$ eV, $V_i \propto E^{1/3}$, $\theta_D^b(\text{As}) = \theta_D^s(\text{As}) =$

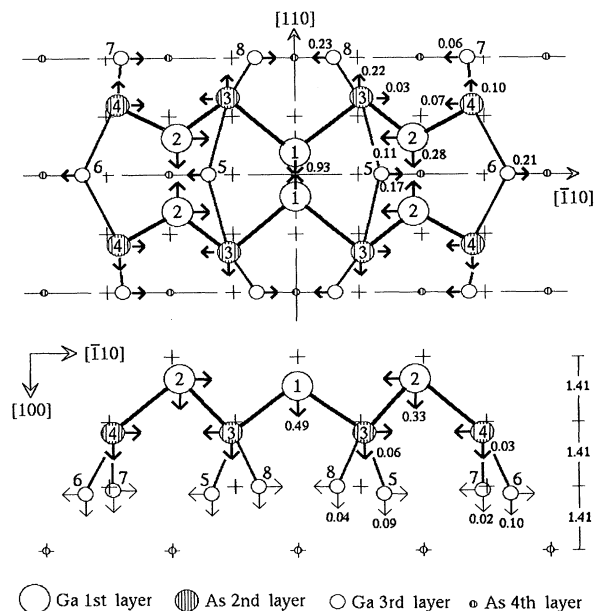$\bigcirc$ Ga 1st layer   ⬚ As 2nd layer   ◯ Ga 3rd layer   ⊙ As 4th layer

FIG. 2. Top and lateral views of the geometry deduced in this work for the GaAs(100)-$c(8 \times 2)$-Ga. Ideal atomic bulk sites are indicated by crosses, while arrows point along the direction of each atomic displacement. The quantities adjacent to the arrows give their magnitude. The atomic numbering is that used in Fig. 1 (model A). All quantities are in Å.

200 K, $\theta_D^b(\text{Ga}) = 179$ K, and $\theta_D^s(\text{Ga}) = 160$ K. The agreement can be visualized in Fig. 3.

Other relevant R-factor values [29] for this geometry are $R_{\text{VHT}} = 0.32$ and $R_{\text{ZJ}} = 0.26$. In order to compare with previous LEED studies on open semiconductor surfaces of great complexity, we recall that Tong et al. achieved a value of $R_{\text{VHT}} = 0.34$ for the Si(111)-(7 × 7) [22], which indicates a similar level of agreement to that obtained here. These relatively high R-factor values are most probably related to the muffin-tin potential used to obtain the atomic phase shifts. This kind of potential will not, in general, model correctly the high bond directionality in a semiconductor, this effect being enhanced at open surfaces [30], such as the present one. The fact that integer- and fractional-order beams yield the same level of agreement ($R_{\text{AV}} = 0.51$ and $R_{\text{AV}} = 0.48$, respectively) seems to corroborate this assumption. Further causes of error can be deeper layer relaxations or the existence of anisotropic atomic vibrations, but the system is far too complex to be treated via the concept of split positions [31]. However, and based on our experience, it is our belief that these corrections will not modify significantly the location of the R-factor minimum in the parameter space, which is the important point here.

There are two main features worth discussing in the geometry represented in Fig. 2. On the one hand, the central Ga atoms (Ga1) appear completely dimerized ($d_{\text{Ga1-Ga1}} = 2.14$ Å), suffering a drastic reduction (0.49 Å) in their height with respect to the As atoms to which they bond (As3). This contraction tends to preserve the Ga1-As3 bond length, although a small expansion (4%) is envisaged, and can be attributed to a weakening of the Ga1 back bonds in favor of the tight Ga1-Ga1 bonding. On the other hand, the four adjacent Ga atoms (Ga2) hardly dimerize ($d_{\text{Ga2-Ga2}} = 3.44$ Å), and their contraction normal to the surface is consequently smaller (0.33 Å). Their bond lengths to the As3 and As4 in the second layer are contracted by -9% and -4%, respectively, which can be interpreted as a reinforcement of back bonds as a result of the weak Ga2-Ga2 interaction.

The semidimerization of the Ga2 seems to violate Pashley's electron counting rule [32]. Assuming the transfer of 1/2 electron from each surface Ga to the As4 in order to fill the dangling bond (DB) of the latter [32], the apparent absence of a Ga2-Ga2 bond would leave one DB per Ga2 occupied by one electron; in principle, an energetically unfavorable situation. However, there exists recent experimental evidence of surface Ga atoms that do not dimerize [33], but only relax towards the bulk,
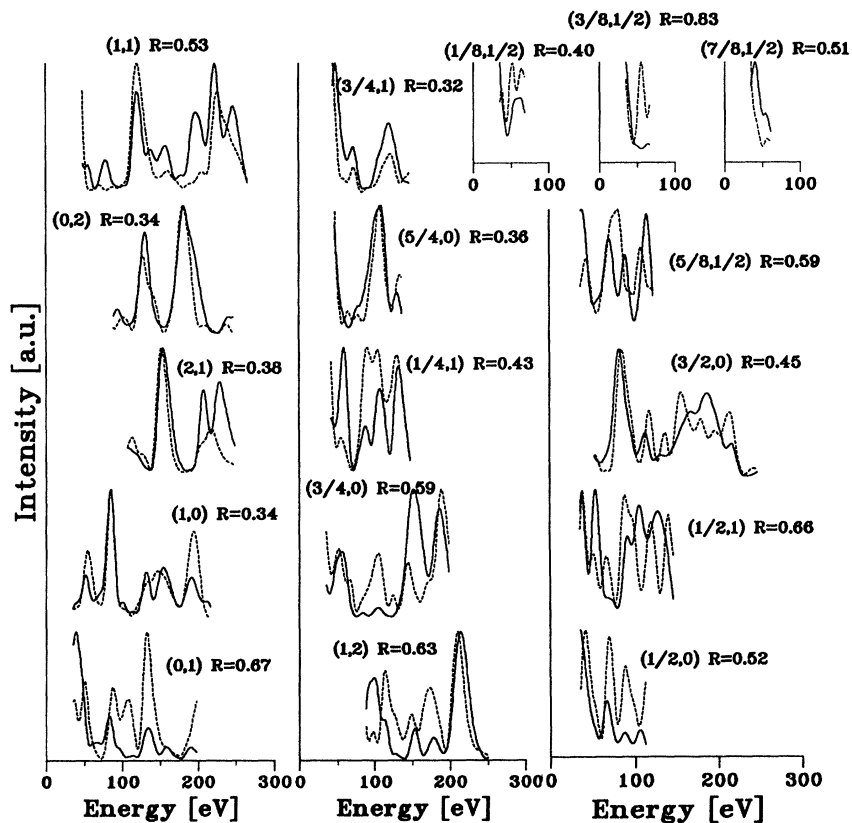

FIG. 3. Experimental (solid lines) and theoretical (dashed lines) I-V curves for the optimized structure shown in Fig. 2. Each beam is accompanied by its individual R_{AV} value.

in agreement with the behavior found here. Therefore one may anticipate that the energetics associated to Ga dimers is not as crucial as that of As atoms for the anion terminated surfaces. This, in turn, also offers an explanation to the smooth transition from the (4×1)-Ga structure at 770 K towards the $c(8 \times 2)$-Ga that appears at 800 K [7,17]. Presumably, then, the formation of a three Ga-dimer structure would imply too high a strain to be compensated by the small energy reduction introduced by the dimerization. Instead, the Ga2 will undergo a rehybridization towards an sp^2 configuration (the increase in the As3-Ga2-As4 bond angle suggests this situation [33]). Additionally, Northrup and Froyen [16] pointed out the important role in the surface stability played by the electrostatic energy at the surface. In this sense, the geometry given in Fig. 2 will always yield a smaller Ga-Ga repulsive energy than a fully dimerized model.

Although our surface preparation technique differs from that used by Skala et al. [13] and Xue et al. [14] and, therefore, the $c(8 \times 2)$ phases might not be the same, the filling of the As4 DB explains the bright rows found by these authors for the occupied states STM images. On the other hand, our model is in complete agreement with the results of Schweitzer et al. for the InSb(100)-$c(8 \times 2)$-In, also prepared by an IBA method [34]. Furthermore, the width of the bright rows for the unoccupied states images [13] is consistent with our three dimer model.

Finally, the presence of two different chemical states for the Ga atoms (Ga1 and Ga2) can explain the existence of two surface peaks in the PES spectra for the Ga $3d$ core level [8,10], while the single surface peak for the As $3d$ can be attributed to the As4 atoms.

In summary, we have performed the first crystallographic study by LEED on a GaAs(100) surface: the $c(8 \times 2)$-Ga prepared by SIBA. Out of the three models considered, the β phase (three adjacent dimers and one dimer vacancy) yielded an agreement significantly better than the rest. From this study, it is concluded that the two middle Ga atoms suffer a full dimerization, but this dimerization is much more subtle for the other four lateral Ga atoms.

---

*Present address: Lawrence Berkeley Laboratory, Berkeley, CA 94720.

[1] A. Y. Cho, J. Appl. Phys. **47**, 2841 (1976).

[2] For a general review, see A. Kahn, Surf. Sci. **299/300**, 469 (1994), and references therein.

[3] J. M. McCoy et al., Phys. Rev. B **48**, 4721 (1993); Y. Ma et al., Surf. Sci. **289**, 47 (1994); T. Hashizume et al., Phys. Rev. Lett. **73**, 2208 (1994).

[4] M. A. Van Hove and S. Y. Tong, *Surface Crystallography by LEED* (Springer-Verlag, Berlin, Heidelberg, New York, 1979).

[5] D. J. Frankel et al., J. Vac. Sci. Technol. B **5**, 1113 (1987).

[6] D. K. Biegelsen et al., Phys. Rev. B **41**, 5701 (1990).

[7] M. A. Mendez et al., Surf. Sci. **251/252**, 145 (1991).

[8] G. Le Lay et al., Phys. Rev. B **43**, 14301 (1991).

[9] R. Duszak et al., J. Vac. Sci. Technol. B **10**, 1891 (1992).

[10] I. M. Vitomirov et al., J. Vac. Sci. Technol. B **10**, 1898 (1992).

[11] W. Chen et al., J. Vac. Sci. Technol. B **10**, 1886 (1992).

[12] J. Falta et al., Phys. Rev. Lett. **69**, 3068 (1992); J. Falta et al., Phys. Rev. B **48**, 5282 (1993).

[13] S. L. Skala et al., Phys. Rev. B **48**, 9138 (1993).

[14] Q. Xue et al., Phys. Rev. Lett. **74**, 3177 (1995).

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

[16] J. E. Northrup and S. Froyen, Phys. Rev. B **50**, 2015 (1994).

[17] F. J. Palomares et al., J. Vac. Sci. Technol. A **9**, 939 (1991).

[18] A. van Oostrom, J. Vac. Sci. Technol. **13**, 224 (1976).

[19] A. Wander, J. B. Pendry, and M. A. Van Hove, Phys. Rev. B **46**, 9897 (1992).

[20] For model B in Fig. 1, the dimerization of Ga6 atoms was not considered since it would break the *pmm* symmetry (these atoms were only allowed to relax along the surface normal). However, the effect of averaging two domains will yield similar results to a nondimerized model for Ga6 atoms, especially if one considers the low LEED sensitivity to lateral displacements.

[21] M. A. Van Hove, R. Lin, and G. A. Somorjai, Phys. Rev. Lett. **51**, 778 (1983).

[22] S. Y. Tong et al., J. Vac. Sci. Technol. A **6**, 615 (1988); H. Huang et al., Phys. Lett. A **130**, 166 (1988); W. Moritz, J. Phys. C **17**, 353 (1984).

[23] J. B. Pendry, J. Phys. C **13**, 937 (1980).

[24] G. Kleinle et al., Surf. Sci. **219**, L637 (1989).

[25] P. J. Rous et al., Phys. Rev. Lett. **57**, 2951 (1986).

[26] P. J. Rous et al., Surf. Sci. **226**, 15 (1990); A. Wander et al., Phys. Rev. Lett. **67**, 626 (1991).

[27] J. Cerdá, Ph.D. thesis, Universidad Autónoma de Madrid, 1995.

[28] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).

[29] M. A. Van Hove et al., Surf. Sci. **64**, 85 (1977); E. Zanazzi and F. Jona, *ibid.* **62**, 61 (1977).

[30] J. V. Peetz and W. Schattke, J. Electron Spectrosc. Relat. Phenom. **68**, 167 (1994).

[31] H. Over, W. Moritz, and G. Ertl, Phys. Rev. Lett. **70**, 315 (1993).

[32] M. D. Pashley, Phys. Rev. B **40**, 10481 (1989).

[33] A. R. Avery et al., Phys. Rev. B **50**, 8098 (1994).

[34] M. O. Schweitzer et al., Surf. Sci. **280**, 63 (1993).