RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 12 15 DECEMBER 1985

Atomic geometry of the 2×2 GaP(111) surface

G. Xu, W. Y. Hu, M. W. Puga, and S. Y. Tong
Department of Physics and Laboratory for Surface Studies, University of Wisconsin–Milwaukee, Milwaukee, Wisconsin 53201

J. L. Yeh, S. R. Wang, and B. W. Lee
Electrical Engineering Department, Rutgers University, Piscataway, New Jersey 08854

(Received 18 September 1985)

Integral and fractional order beam low-energy electron-diffraction intensity-voltage (I-V) data have been taken on a bombardment-annealed GaP(111)-(2×2) surface. We have compared these data with calculated I-V curves using a dynamical multiple scattering theory and found very good agreement for the following model: One out of every four Ga surface atoms is missing and the surface Ga-P bilayer is almost coplanar. Surface and deeper-layer atoms undergo vertical and lateral displacements from bulk positions. Similar results in other systems suggest that the vacancy model applies on the (111) face of many compound semiconductors.

Recently there has been considerable interest in the reconstruction structure of polar faces of compound semiconductors. For the first time, a quantitative structure has been proposed[1] for the (2×2) Ga-rich (111) face of GaAs. The model involves a quarter monolayer of Ga atoms missing from the outermost atomic plane. The remaining Ga atoms in that plane and the As atoms in the plane below undergo large vertical and lateral atomic displacements. These displacements are driven by the rehybridization of Ga and As surface orbitals. The positions of the surface and subsurface atoms were determined by dynamical low-energy electron-diffraction (LEED) intensity-voltage (I-V) spectra analysis, and the model was confirmed by results of other independent studies.[2,3]

In this Rapid Communication, we report results of structural determination of the (111) surface of another III-V compound semiconductor: GaP. The results again indicate a vacancy-stabilized structure, with one quarter of the surface Ga atoms missing. The orbitals on the remaining surface Ga atoms rehybridize into sp^2 orbitals, while those in the nearest-neighbor p atoms rehybridize into s^2p^3 orbitals. This result is consistent with the reconstruction model found on GaAs(111) and, together with results of a recent x-ray scattering analysis[4] on the InSb(111) surface, strongly suggests that the (111) surface of many III-V compound semiconductors undergoes the same (2×2) vacancy-stabilized reconstruction.

The LEED study was done by analyzing ten beams: five integral beams (1,0; 0,1; 1,1; 2,0; and 0,2) and five half-order beams ($\frac{1}{2}$,0; 0,$\frac{1}{2}$; 1,$\frac{1}{2}$; $\frac{3}{2}$,0; and 0,$\frac{3}{2}$). The I-V data were taken on a GaP(111) surface which was polished and chemically etched to differentiate the (111) Ga-rich face from the $(\bar{1}\bar{1}\bar{1})$ P-rich face. Using an etching solution of $HCl:HNO_3:H_2O = 3:1:4$ and an etching time of about two minutes, the (111) face showed dislocation pits with hexagonal shapes. The $(\bar{1}\bar{1}\bar{1})$ face did not show this feature, due to the high etching speed.

We then placed the sample in an ultrahigh vacuum chamber (3×10^{-10} torr) with the (111) face towards the electron gun. A bombard-annealing cycle was used to clean the sample using Ar ions at 500 eV and temperatures of 550 °C. After several cycles, the surface showed no detectable oxygen signal and a very minute trace of carbon (<1 in 10^2 atoms) under Auger electron spectroscopy.

A sharp and stable (2×2) pattern was observed and it was easily reproduced. Scanning over the sample, we found that every place in the surface showed a (2×2) pattern with a threefold symmetry. This indicated that the surface structure has a true (2×2) periodicity and the LEED pattern was not made up of domain averages of patches with lower symmetry [e.g., three domains of (2×1) structures].

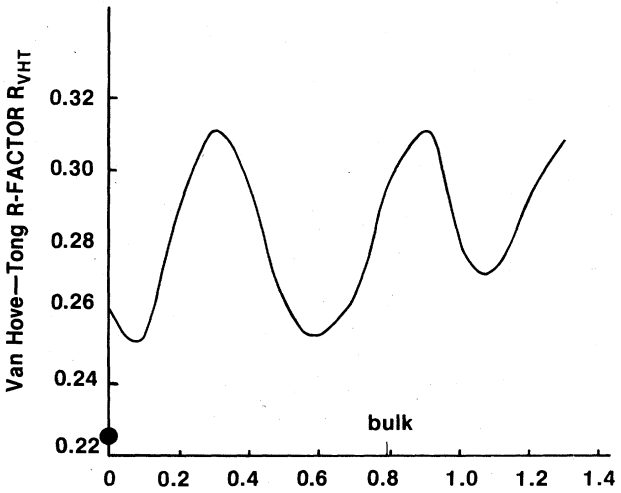
The experimental data show that the energy width of the half-order beams were very similar to those of the integral-order beams. This indicates that the (2×2) new periodicity propagates at least a few layers into the bulk, instead of appearing only in the surface layer. For the theoretical analysis, we used a fully convergent multiple scattering program of LEED.[5] All the dynamical inputs were left the same as those used for the GaAs(111) surface,[6] with the obvious exception that different phase shifts were used for the Ga and P potentials. Thus only structural parameters were allowed to vary in optimizing the agreement between calculated and measured I-V curves. The R-factors of Van Hove, Tong, and Elconin,[7] Tong and Lau,[8] and Zanazzi and Jona[9] were used in the intensity spectra analysis. The calculation used 6 partial waves and 229 beams, and a temperature correction with surface and bulk root-mean-square vibration amplitudes of 0.13 Å. The C_{3v} symmetry among beams was used to reduce the 229 unsymmetrized beams down to 47 symmetrized beams. The inner potential (V_0) is a constant (−9 eV) at incident energies above 100 eV. Below 100 eV it is energy dependent with the functional form

$$V_0(E) = -9 - 0.07(100 - E) \text{ eV} . \quad (1)$$

The inelastic damping (V_I) also has an energy dependence given by the formula

$$V_I(E) = 3.8\left[\frac{E + V_0(E)}{90 + V_0(E)}\right]^{1/3} \text{eV} . \quad (2)$$

An important parameter in the structural search is d_1, the spacing between the first (Ga) and second (P) atomic planes. We first varied its value, keeping a (1×1) structure and all other structural parameters at bulk values. Figure 1



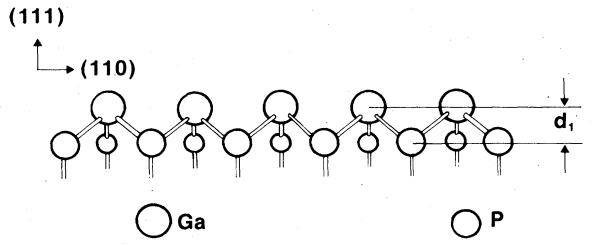


FIG. 1. Plot of R factor vs the surface bilayer spacing for GaP(111). Three minima occur at $d_1 = 0.06$, 0.59, and 0.79 Å. The solid circle on the y axis indicates the R factor value of the optimal structure listed in Table I. Lower figure indicates the first bilayer atoms in an ideal bulk structure.

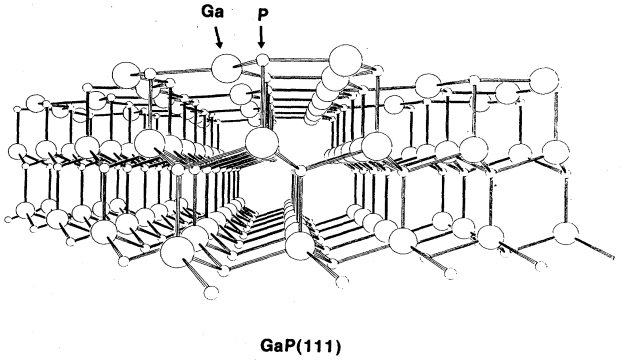


FIG. 2. Schematic side view of vacancy-stabilized GaP(111) surface with surface atoms at location indicated in Table I. The surface bilayer is almost coplanar, with tetrahedrally bonded P atoms 0.09 Å below the outer surface atoms.

shows the dependence of R_{VHT} with d_1, using comparison between theory and experiment for the five integral beams (no half-order beams were used at this stage, since we were testing a 1×1 structure). From Fig. 1, it is clear that we can rule out the bulk spacing (0.79 Å). There are two regions where R_{VHT} has minima ($d_1 = 0.59$ and 0.06 Å). Further search near the $d_1 = 0.59$-Å minimum produced very poor (i.e., large) R_{VHT} values ($R_{VHT} \sim 0.3$ to 0.4). The optimal structure was found by searching in the vicinity of the minimum near $d_1 = 0.06$ Å. By introducing lateral and vertical displacements on surface and subsurface atoms, and by removing one-quarter Ga atoms from the surface, the final R_{VHT} factor was 16% below the minimum of the curve in Fig. 1 (see solid circle at $d_1 = 0$ Å).

A side view of the final structure is seen in Fig. 2, showing an almost flat GaP(111) surface. The final structural parameters are listed in Table I, and Figs. 3 and 4 show the

TABLE I. Atomic positions, with origin at the (bulk) missing atom, for the unreconstructed and reconstructed structures of GaP(111). The x, y, and z axes are along $(1\bar{1}0)$, $(11\bar{2})$, and $(\bar{1}\,\bar{1}\,\bar{1})$ directions, respectively, with the crystal on the $+z$ side.

			Unreconstructed surface			Reconstructed surface		
			z	x	y	z	x	y
First bilayer	Ga	1	0.000	0.000	0.000		missing	
		2	0.000	1.927	−3.338	0.746	1.809	−3.406
		3	0.000	3.854	0.000	0.746	3.854	0.136
		4	0.000	1.927	3.338	0.746	2.045	3.270
	P	5	0.787	1.927	1.113	0.746	1.728	0.998
		6	0.787	3.854	−2.225	0.836	3.854	−2.225
		7	0.787	5.781	1.113	0.746	5.980	0.998
		8	0.787	3.854	4.450	0.746	3.854	4.680
Second bilayer	Ga	1′	3.147	3.854	−2.225	3.237	3.854	−2.225
		2′	3.147	5.781	−5.563	3.127	5.781	−5.563
		3′	3.147	7.708	−2.225	3.127	7.708	−2.225
		4′	3.147	5.781	1.113	3.127	5.781	1.113
	P	5′	3.934	5.781	−1.113	3.934	5.781	−1.113
		6′	3.934	7.708	−4.450	3.934	7.708	−4.450
		7′	3.934	9.635	−1.113	3.934	9.635	−1.113
		8′	3.934	7.708	2.225	3.934	7.708	2.225

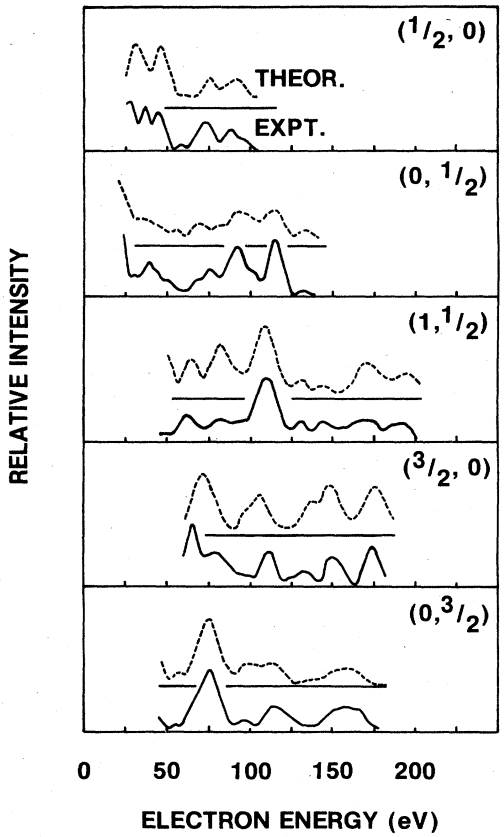


FIG. 3. Comparison between calculated I-V curves with experiment, for half-order beams.

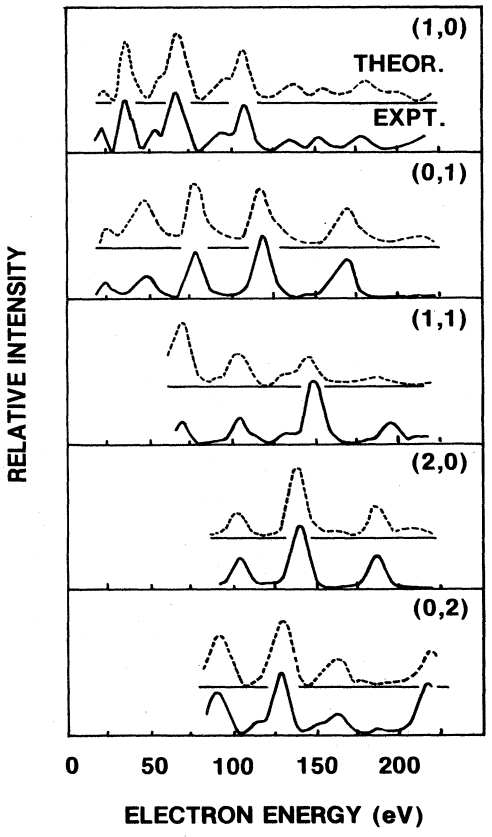


FIG. 4. Comparison between calculated I-V curves with experiment, for integral-order beams.

agreement obtained between calculated and measured (I-V) curves. Such good agreement, corresponding to our optimal structure, has an R factor of $R_{\mathrm{VHT}}=0.19$ for the integral beams and $R_{\mathrm{VHT}}=0.25$ for the half-order beams. The combined R factor for all beams is $R_{\mathrm{VHT}}=0.21$ (different beams are weighted differently because of the different energy range of the measured data). This final value of the R factor is indicated as an extra point in Fig. 1, the solid circle on the y axis of the figure. The very small d_1 value in the final structure is significant. It indicates that the Ga surface atoms are almost entirely rehybridized into planar sp^2 bonds. This coplanarity is indicative of vacancy formation, since in each (2×2) unit cell three Ga atoms rehybridize into sp^2 bonds. This can be achieved by having the fourth Ga atom missing, creating three P atoms with dangling bonds to accept the (three) additional electrons. If it were a buckled model, and the fourth Ga atom was simply raised on the surface, it would have to receive the (almost) three electrons transferred from the planar Ga atoms. This would result in a much less complete rehybridization and the structure would have less coplanarity than the one we have determined.

The numbers in Table I show that the surface is almost completely relaxed. Taking into consideration the sp^2 rehybridization of Ga and the p rehybridization of P at the surface, we find the surface bonds to be a sp^2-p mixture with a bond length 2.8% smaller than the bulk. The P back bond (connecting the P in the new diatomic surface with the Ga in the layer below) is a sp^3-p mixture, with a length 1.1% larger than the bulk. The Ga back bond (connecting the surface Ga atom to the tetrahedrally bonded P), is a mixture of sp^2 and sp^3 bonds with a length 0.12% larger than the bulk.

Finally, in 1966 Pretzer and Hagstrum[10] concluded, after studying the GaAs(110) and (111) faces by ion neutralization experiments, that the electronic configuration of the two surfaces should be very similar. This fact, which was rather puzzling at the time, is well explained by the vacancy model. The formation of a vacancy allows electronic rehybridization of the (111) surface of III-V semiconductors. Basically this surface is transformed into one which locally resembles a 110 surface (with an equal number of dangling bonds for type-III and type-V atoms), and therefore a similar driving mechanism stabilizes both the (111) and (110) surfaces.

This work is supported in part by the U.S. Department of Energy under Grant No. DE-FG02 84ER45076.

[1]S. Y. Tong, G. Xu, and W. N. Mei, Phys. Rev. Lett. **52**, 1693 (1984).
[2]D.J. Chadi, Phys. Rev. Lett. **52**, 1911 (1984).
[3]M. Alonso, F. Soria, and J. L. Sacedon, J. Vac. Sci. Technol. A **3**, 1598 (1985).
[4]J. Bohr, R. Feidenhans'l, M. Nielsen, M. Tonney, R. L. Johnson, and I. K. Robinson, Phys. Rev. Lett. **54**, 1275 (1985).
[5]S. Y. Tong and M. A. Van Hove, Phys. Rev. B **16**, 1459 (1977).
[6]S. Y. Tong, G. Xu, W. Y. Hu, and M. W. Puga, J. Vac. Sci. Technol. B **3**, 1076 (1985).
[7]M. A. Van Hove, S. Y. Tong, and M. H. Elconin, Surf. Sci. **64**, 85 (1977).
[8]S. Y. Tong and K. H. Lau, Phys. Rev. B **25**, 7382 (1982).
[9]E. Zanazzi and F. Jona, Surf. Sci. **62**, 61 (1977).
[10]D. D. Pretzer and H. D. Hagstrum, Surf. Sci. **4**, 265 (1966).