Vacancy-Buckling Model for the (2×2) GaAs(111) Surface

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(Received 20 January 1984)

A vacancy-buckling model is proposed for the (2×2) structure of the GaAs(111) surface. The model is confirmed by analysis of low-energy electron diffraction spectra. A reconstruction mechanism, basic to III-V compound surfaces, is proposed which favors equal numbers of dangling bonds on the nearest Ga and As neighbors. This model explains the (2×2) and (1×1) periodicities observed on (111) and (110) surfaces, respectively.

PACS numbers: 68.20.+t

The structure of the polar faces of III-V compound semiconductors has remained an unknown after many years of intense study. Here, each atomic plane is monopolar, and the crystal is made up of alternating planes of group III and group V atoms. Haneman's buckling model[1] was introduced in 1961 to explain the (2×2) structure found commonly on the (111) and $(\bar{1}\bar{1}\bar{1})$ faces of diamond and zinc-blend structure semiconductors. According to the original idea, three out of every four surface atoms recede toward the bulk, and the remaining one quarter of surface atoms are raised upward. The atomic displacements are accompanied by orbital rehybridization which leaves occupied *s*-type dangling hybrids on the raised atoms and nearly empty hybrids on the inwardly receded atoms.

A major difficulty of the buckling model when applied to the polar faces of III-V compounds is that the buckling is between atoms of the same kind. Thus, on GaAs(111), the surface Ga atoms must undergo orbital rehybridization of *different* kinds. If the amount of orbital rehybridization is large, the buckling is not cost effective because of the large intra-atomic Coulomb repulsion on the upwardly raised atoms.

We propose here a different model for the (2×2) structure of the (111) face of III-V compound semiconductors. Our model has one quarter of surface (group III) atoms missing. The remaining three quarters of surface atoms undergo buckling distortions with a same number of group V atoms in the atomic plane *below*. In other words, the buckling is now between nearest-neighbor atoms of different kinds, in a configuration interestingly similar to that found on the (110) surface. The group III atoms that remain on the surface recede toward the bulk, their atomic orbitals rehybridize to form sp^2-type bonds. The group V atoms in the layer below are pushed sideways and outwards, producing *s*-type and near 90° separated *p*-type bonds, reminiscent of the reconstructed (110) surface.

We find that the "vacancy-buckling" model explains the structure of the (2×2) GaAs(111) surface. The structural determination was done by analysis of low-energy electron diffraction (LEED) intensity-voltage data using a fully convergent multiple-scattering method.[2] A slab of twenty atomic layers (i.e., ten Ga-As bilayers) was used and the top two bilayers contained up to eight atoms per unit cell. We show in Fig. 1 a top view of our model. The broken arrows indicate the (2×2) unit cell. Three atomic layers are shown: *A, B,* and *C* denote surface layer Ga atoms; *a, b, c,* and *d* denote As atoms in the layer immediately below. In the third layer, Ga atoms are denoted by the smallest circles (open and hatched). A side view of the model, taken along section *XX'* and viewed from "*s*" of Fig. 1 is shown in Fig. 2. Note that after reconstruction, there are five atomic planes

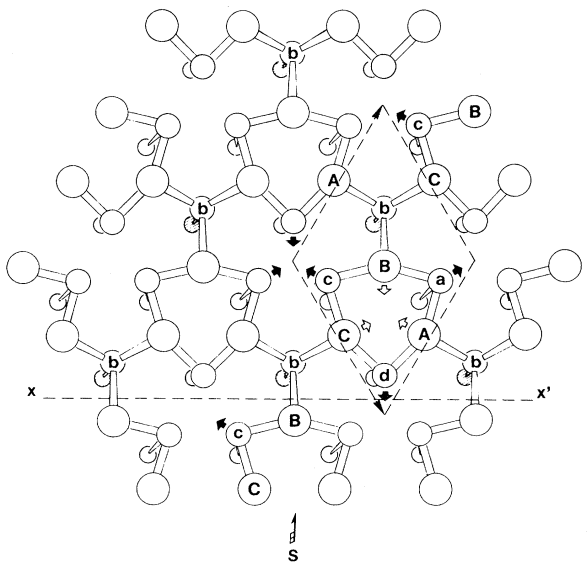

FIG. 1. Top view of (2×2) vacancy-buckling (VB) model.

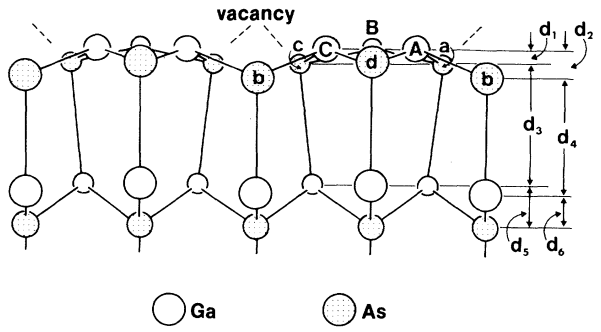

FIG. 2. Side view of VB model: $d_1 = 0.07$ Å, $d_2 = 0.20$ Å, $d_3 = 2.48$ Å, $d_4 = 2.44$ Å, $d_5 = 0.83$ Å, and $d_6 = 0.74$ Å.

having the (2×2) periodicity. The atomic displacements, determined from our dynamical LEED analysis, are listed in Table I, with $(+)$ and $(-)$ numbers denoting vertical displacements away and towards the bulk, respectively.

The polished GaAs(111) sample was cleaned by 0.5-keV Ar^+ beam bombardment and annealed to $\sim 500\,^{\circ}C$ in an UHV chamber of 3×10^{10} Torr. A (2×2) LEED pattern was observed and the pattern was found to be very stable. Intensity-energy curves were taken for ten beams (five integral-order and five fractional-order spots).[3] A fully convergent multiple-scattering theory[2] was used to calculate intensity-energy curves and these were compared with the data. Because of the large number of ways surface atoms can displace, we used the following procedure: We varied the first Ga-As bilayer spacing by vertically displacing the surface atoms up and down. We compared calculated

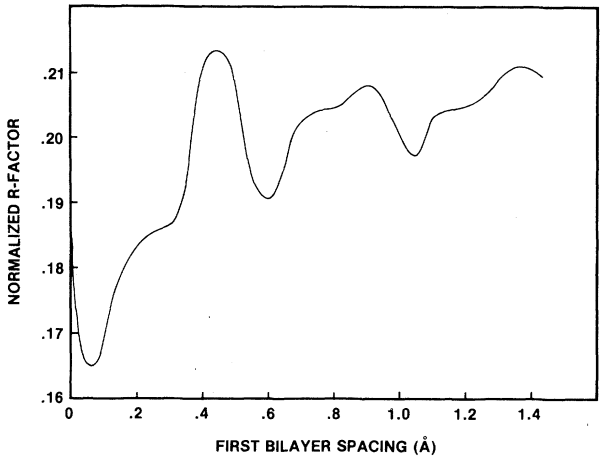

FIG. 3. Plot of R factor vs bilayer spacing.

intensity-energy curves with the measured curves for the five integral-order beams. The comparison was done by visual inspection and by the use of a normalized R factor.[4] We plotted in Fig. 3 R-factor values versus first bilayer spacing d and found a deep minimum at $d = 0.06$ Å, and two other local minima at 0.6 and 1.05 Å. The bulk bilayer spacing is $d = 0.816$ Å. We then searched in regions around the three minima with the introduction of vacancies in the top layer and buckling distortions in the top three layers.

In Fig. 4, we show the comparison between theory and experiment for two integral-order beams for the optimal vacancy-buckling geometry. We obtained excellent agreement in the number of peaks and the peak positions.

TABLE I. Atomic displacements from bulk positions for the optimal vacancy-buckling model.

	Atoms L = layer	Notations in Fig. 1	Vertical displacement (Å) up(+) down(−)	Lateral displacement (Å)
First bilayer	$\frac{1}{4}$ L Ga	Missing		
	$\frac{3}{4}$ L Ga	A,B,C	−0.706	0.10 along hollow arrows
	$\frac{3}{4}$ L As	a,c,d	0.04	0.28 along solid arrows
	$\frac{1}{4}$ L As	b	−0.08	0.0
Second bilayer	$\frac{3}{4}$ L Ga	Open circles	0.01	0.0
	$\frac{1}{4}$ L Ga	Hatched circles	−0.08	0.0
	1 L As	Not shown	0.0	0.0

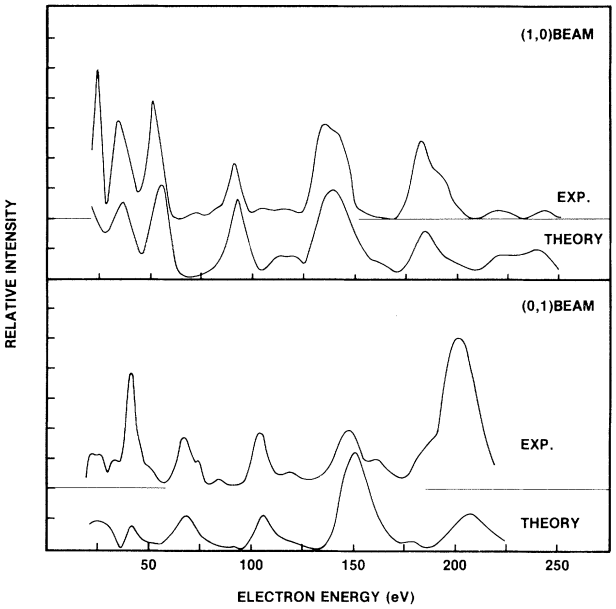

FIG. 4. Comparison between calculated intensity-energy curves with experiment, for the optimal VB geometry listed in Table I.

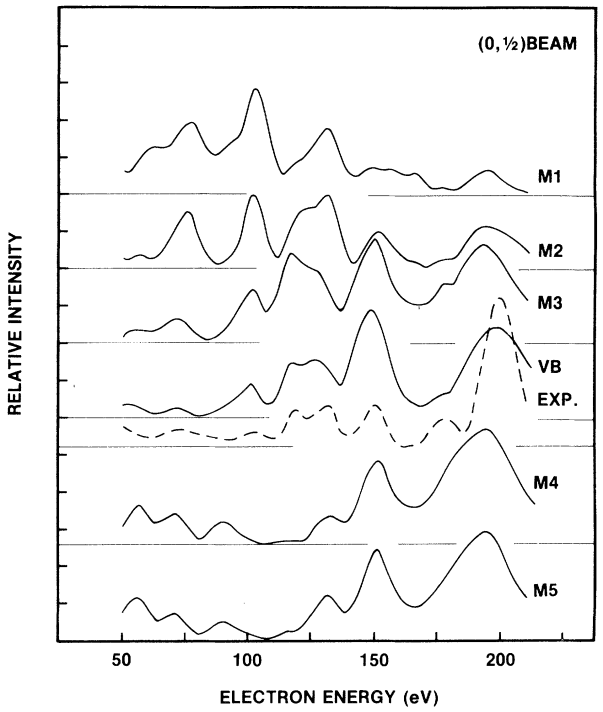

FIG. 5. Comparison between calculated intensity-energy curves with experiment, for six structural models.

The intensity-energy curves for the fractional-order beams are sensitive to buckling distortions that produce a (2×2) periodicity in each atomic layer. This is because to lowest scattering order, a (1×1) layer does not scatter electrons into the fractional-order spots. We show in Fig. 5 the comparison between experimental and calculated intensity-energy curves for the $(0\ \frac{1}{2})$ beam in the energy range 50–220 eV for six different atomic arrangements: Model $M1$ has $\frac{1}{4}$ layer vacancies in the surface Ga layer plus a vertically compressed surface bilayer with $d=0.07$ Å. Model $M2$ includes the displacements of $M1$ but has additional lateral shifts for Ga and As atoms in the first bilayer. Model $M3$ includes the displacements of $M2$, but with further vertical shifts of $\frac{1}{4}$ layer As in the first bilayer towards the bulk and shifts of $\frac{3}{4}$ layer As towards the surface. Model VB (vacancy buckling) is our final structure for which the atomic displacements are listed in Table I. It includes atomic displacements of $M3$, but with additional shifts of $\frac{3}{4}$ layer Ga atoms in the second bilayer towards the surface and shifts of $\frac{1}{4}$ layer Ga atoms towards the bulk.

Also shown in Fig. 5 are two other models, $M4$ and $M5$, in which each vacancy is filled by an As atom (the "substitutional model") and a Ga atom (the "buckling only" model), respectively. In both cases, we used R-factor values to determine the optimal binding distances of the As and the Ga atom. We found that, for both cases, the As or Ga atom was raised 1.21 Å above the other three Ga atoms in the unit cell.

The sensitivity of the five fractional-order beams to the six different models is shown in Fig. 6. We plot R-factor values of the fractional-order beams for each of the six models. We found that the optimal "vacancy-doubling" model (VB) has the smallest R factor, which is 58.6% less than that of $M1$. Moreover, the "vacancy-buckling" model gives an R factor which is 13.6% and 17.5% less than those of the optimal "As-substitutional" model ($M4$) and "buckling-only" model ($M5$), respectively.

Although vacancy and substitutional[5] models have been suggested in the past as possible structures on polar faces of III-V semiconductors, such speculations have never been quantitatively verified. This study presents the first quantitative analysis that demonstrates the existence of vacancies on a semiconductor surface. The complicated atomic displacements are determined. An important component of our model is the buckling that follows the creation of a vacancy. The buckling is most favorable if there are *equal numbers of dangling bonds on the nearest Ga and As neighbors.*[3] This

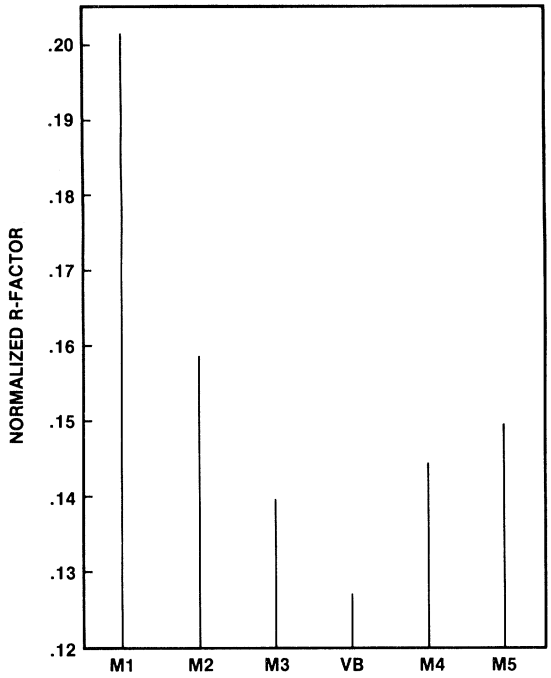

FIG. 6. Normalized R-factor values for six structural models.

"preference" explains why the stable reconstructed surface has a (2×2) periodicity on (111) and a (1×1) periodicity on the (110) surface. On GaAs(111), each surface Ga atom has one dangling bond. By removing one surface Ga atom/unit cell, three As dangling bonds are created. To balance these, the new unit cell must then have three surface Ga atoms—hence the (2×2) periodicity. From Fig. 1, it is clear that in each (2×2) unit cell, every Ga atom with a dangling bond is *bonded* to an As atom, which also has a dangling bond. This configuration promotes orbital rehybridization via buckling and the total energy is minimized.

On the (110) surface, the bulk-terminated surface already has equal numbers of nearest-neighbor dangling bonds of each type. Hence, the stable reconstructed structure retains the (1×1) periodicity.[5-15] The atomic displacements of this surface were earlier determined by dynamical LEED analysis.[9-11]

The authors wish to acknowledge valuable discussions with D. J. Chadi, J. E. Rowe, R. J. Mrstik, and M. A. Van Hove. This work was supported by National Science Foundation Grant. No. DMR-81-01203.

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