

Surface Structure of α -Ga(010)

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We have determined the surface structure of α -Ga(010) near its melting point using x-ray diffraction. Of the two possible ideal ways to form the (010) surface, we find that the true surface is formed by cutting through dimer bonds (i.e., between metallic bilayers). The contraction of the metallic bonds and the expansion of the covalent bonds at the surface imply that the surface is more metallic than the bulk. Our results suggest that α -Ga is fundamentally composed not of Ga_2 dimers, but of corrugated metallic bilayers which can be modeled as deltahedral clusters. [S0031-9007(98)06610-1]

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Atoms at surfaces face lower coordination than their bulk counterparts, often accommodating this change in environment by displacing from locations given by a simple truncation of the bulk. For clean metal surfaces, the loss of coordination results in a tendency for the outermost plane of atoms to relax inwards, allowing those atoms to become more fully bathed in the electronic sea. For semiconductor surfaces, it may result in dangling covalent bonds, a high-energy situation often resolved by reconstructions which minimize the number of dangling bonds across the surface's unit cell, usually with a periodicity which is some multiple of bulk unit cells. The stable phase of gallium at low pressure, labeled α -Ga, is commonly thought to contain both metallic and covalent bonds. Investigations of α -Ga surfaces lend insight to the unusual metallic-covalent duality of this material, and hence to metal-insulator transitions in general. Here we report an experimental determination of the three-dimensional structure of α -Ga(010) surface.

Several recent x-ray reflectivity studies have probed the surface structure of (fully metallic) liquid Ga, finding layering of the liquid at the free surface and in contact with a hard wall. For the liquid Ga/vacuum interface, Regan *et al.* [1] measured a layering with spacing $d \sim 2.6$ Å (consistent with atomic layering), with an exponential decay length of about 6 Å; these lengths remained remarkably constant over the temperature range $T = 295$ K (supercooled liquid) to 443 K. At the liquid Ga/diamond(111) interface, Huisman *et al.* [2] found a layer spacing of $d \sim 3.8$ Å and a decay length of 4 Å.

α -Ga is a semimetal with a low melting point ($T_m = 303$ K). Its orthorhombic crystal structure has $Cmca$ symmetry with $a = 4.5192$ Å, $b = 7.6586$ Å, and $c = 4.5258$ Å [3]. With eight atoms per unit cell, α -Ga is not very dense and its density increases upon melting. One atom is located at $(0, y, z)$, where $y = 0.1539$ and $z = 0.0798$ in fractional coordinates of the unit cell [3]. The seven other atomic positions are determined by the $(8f)$ site symmetry, which places two atoms at each y ,

with $x = 0$ or $\frac{1}{2}$. As seen in Fig. 1, each atom has a total of seven neighbors in the first coordination shell. One of these neighbors is at the surprisingly short distance of 2.465 Å. The pairs of atoms connected by this "dimer" bond (labeled D in Fig. 1) are angled $\pm 17.0^\circ$ from $[010]$, and are generally thought to be bonded covalently, as discussed below. The six next nearest atoms are paired at distances of 2.70, 2.73, and 2.79 Å; the bonds to these atoms are labeled $M1$, $M2$, and $M3$, respectively.

The one short dimer bond is the most prominent feature of the α -Ga structure, implying that the Ga_2 dimer is the fundamental building block of the crystal. Speculation on the covalent nature of the dimer bond has existed since the first accurate α -Ga structure determination [4], but direct evidence has been limited. The electrical conductivity is lowest along the b axis (i.e., the average direction of the

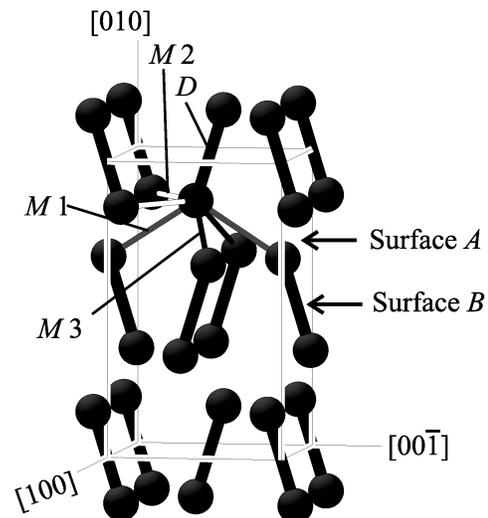


FIG. 1. Bulk structure of α -Ga, showing the seven nearest-neighbor bonds for one of the atoms. The covalent bond labeled D has a length of 2.46 Å; the three pairs of metallic bonds are $M1$, $M2$, and $M3$, and are 2.70, 2.73, and 2.79 Å long, respectively [3]. Bulk truncations to form the two possible (010) surfaces, A and B , are indicated.

dimer bonds) and much greater in the (010) plane [5]; thus, the bonds in the (010) plane (labeled $M1$, $M2$, and $M3$ in Fig. 1) are more metallic than the dimer bonds. Breaking of covalent bonds upon melting may explain the high entropy of melting of α -Ga (almost twice that of metallic β -Ga) [6]. Early calculations by Heine [7] concluded that the short bond length and low-symmetry structure is merely the result of a minimum in the pseudopotential which favors a short bond length despite the large unit cell. However, *ab initio*, total-energy calculations of α -Ga bulk structure [8] found significant charge accumulation in the dimer bonds. Furthermore, electronic band structure calculations [8] predicted a pseudogap in the electronic density of states at the Fermi level, consistent with the semimetallic nature of α -Ga; highly anisotropic band structure at the Fermi surface, consistent with the anisotropic conductivity [5]; and a bonding-antibonding transition at ~ 2.3 eV associated with the covalent bonds, consistent with optical conductivity measurements [9].

For a fresh perspective on the α -Ga bulk geometry, Häussermann *et al.* [10] did not assume the Ga_2 dimer is the building block of α -Ga. Instead, they modeled a two-dimensional net of Ga atoms with the symmetry of a terminally coordinated deltahedral cluster. Within a net, the atoms are connected with metallic bonds, but each atom has one dangling bond left over. To construct a 3D structure, 2D nets are connected at the dangling bonds, forming covalent bonds between the nets. Buckling these nets to an appropriate angle while maintaining $Cmca$ symmetry produces the (slightly idealized) α -Ga structure, succinctly explaining the main structural and electronic properties of bulk α -Ga.

To further understand the properties of this unusual material, we turn to the (010) surface. Because of the low symmetry of bulk α -Ga, two possible (010) surfaces can be created from ideal bulk terminations. As shown in Fig. 1, splitting the metallic bilayer creates surface A , while a cut through the dimer bonds creates surface B . Surface A is created by the breaking of four metallic bonds per surface atom, and B by the breaking of one covalent bond. These two surfaces are separated by one-quarter of a unit cell, and would presumably have very dissimilar properties. According to *ab initio* total-energy calculations by Bernasconi *et al.* [11] the ideal surface of neither A nor B is stable, but the lowest-energy surface is a major rearrangement of surface A : the top layer of dimers is tilted and stretched, significantly decreasing the degree of covalency. The top two atomic layers become metallic, and are comparable to two layers of Ga III (a fully metallic, high-pressure phase of Ga [12]) which self-wets the α -Ga. Although Ga III is face-centered tetragonal, Bernasconi *et al.* argue that two layers of Ga III can deform to match the proposed structure, if the in-plane lattice parameters are appropriately constrained.

Züger and Dürig [13] performed scanning tunneling microscopy (STM) experiments of α -Ga(010), finding the

atoms of the top layer relax significantly in both the x and z directions. (We have relabeled the axes from their paper [13] to be consistent with the crystallographic convention [3].) The degeneracy of the two surface atoms per unit cell is broken, with one shifted 0.05 Å higher than the other, and thus separated by 2.723 Å (slightly less than the bulk $M2$ bond length). STM is inherently limited as a crystallographic tool; its inability to probe below the top layer of atoms does not allow it to differentiate between surfaces A and B . STM is, however, ideal for examining surface “defects.” For example, Züger and Dürig determined that the (010) surface is extremely stable even up to the melting point, without the appearance of any vacancies, adatom diffusion, or step fluctuations. More significantly, a step-height analysis of a slightly miscut (010) surface shows all steps are 3.8 Å high. This distance is one-half the unit cell; no steps of 1.9 Å, or $\frac{b}{4}$, were found, clearly demonstrating that α -Ga(010) terminates as surface A or B , but not a mixture of both.

In order to conclusively differentiate between surfaces A and B , we used surface x-ray diffraction to determine the surface structure. The α -Ga single crystal used in this experiment was grown in UHV conditions, with the (010) surface an as-grown natural facet. Surface x-ray diffraction measurements were performed at beam line X16A of the National Synchrotron Light Source, Brookhaven National Laboratory. A load-lock installed on the surface diffraction chamber [14] allowed introduction of the sample without breaking vacuum (base pressure of chamber $\sim 7 \times 10^{-10}$ Torr for this experiment). The surface was cleaned with repeated cycles of 1 keV Ar ion bombardment, but no annealing, due to the low melting temperature. Using 9.7 keV x rays, 882 structure factors were measured at $T \sim 290 \pm 10$ K. The structure factors, derived from integrated intensities of diffractometer ϕ scans, were corrected for Lorentz and polarization factors and the variation of the illuminated area on the surface. These structure factors were symmetry averaged (with an average agreement factor of 9.5%) to 278 points on ten crystal truncation rods [15], four of which are shown in Fig. 2, along with the A and B bulk terminations and the best fit (described below). With no superstructure reconstruction on this surface, all these rods pass through bulk diffraction peaks.

In our model of the surface, the atoms are allowed to relax from their bulk-defined positions, including the x direction (breaking the bulk’s mirror-plane symmetry in which all atoms are at $x = 0$ or $\frac{1}{2}$). However, the two atoms per unit cell at a given y value remain crystallographically equivalent. Thus, when one atom is displaced by $(+\Delta x, +\Delta y, +\Delta z)$, its partner will move in $(-\Delta x, +\Delta y, -\Delta z)$. Given this degeneracy, our fitting procedure averages intensities over equally probable surface domains with opposite displacements in x and/or z .

Models based on surface A could only give a good fit when the top layer atoms are substantially expanded away from their neighbors and attain unphysically large

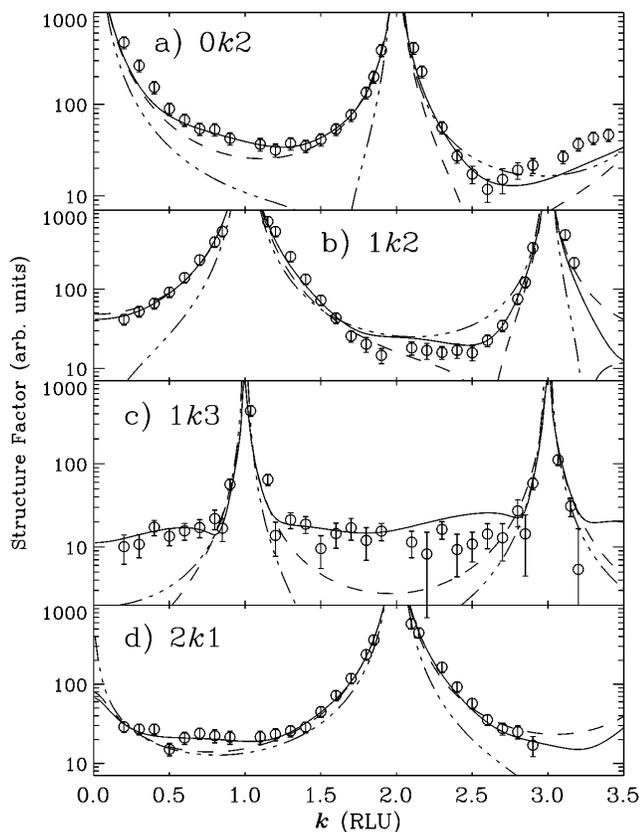


FIG. 2. Four of the ten crystal truncation rods measured. Circles represent data points; solid lines represent the best fit based on a relaxation of surface B . Dashed and dash-dotted lines indicate values for bulk truncations of surfaces B and A , respectively ($\chi_B^2 = 5.5$; $\chi_A^2 = 13.2$). To maintain the crystallographic convention of labeling the α -Ga axes, we break with surface science convention and use k as the continuous variable to index the rods.

Debye-Waller factors, suggesting the *absence* of this layer. In fact, the best fit of the surface is a relaxed version of surface B , with shortened nearest-neighbor metallic bonds and lengthened dimer bonds. In this model, the atoms of the top five layers of the surface were allowed to relax in y and z , and the top three layers could also relax in x . Neither further relaxations nor the breaking of any layer's degeneracy improved our fit.

In addition to thirteen displacive parameters, our model includes an overall scale factor, a roughness factor, and three Debye-Waller parameters. Using a standard formulation for roughness based on a geometric distribution of terrace heights [15], we find a width of $\sqrt{\sigma^2} = 12.7 \pm 1.0 \text{ \AA}$ ($\beta = 0.74$, as defined in Ref. [15]). This large value does not necessarily indicate that α -Ga(010) is an intrinsically rough surface; rather, it is the result of the surface's apparent inability to anneal below its (low) melting point. The constant value of the crystal truncation rods' widths along k indicate that this roughness is not laterally correlated.

Three Debye-Waller parameters were used to model thermal vibrations. All atoms except the two of the top

layer could be assigned to one isotropic Debye-Waller parameter, which was fixed at $B_{\text{bulk}} = 0.4 \text{ \AA}^2$. The two atoms on the top layer needed an anisotropic Debye-Waller factor, separating perpendicular and in-plane vibrations. As expected, the vibrations perpendicular to the surface were significantly enhanced: $B_{\perp} = 9.6 \pm 1.2 \text{ \AA}^2$ vs $B_{\parallel} = 1.43 \pm 0.2 \text{ \AA}^2$. These high values are probably a result of being only 10–20 K below the melting point, although B_{\perp} and the surface roughness are correlated, since both act as q_{\perp} dependent scale factors. Assigning independent Debye-Waller factors to additional atoms neither improved the fit nor altered the refined atomic positions.

Table I lists the in-plane displacements from bulk and vertical layer changes of our refined model, yielding a $\chi^2 = 2.43$. Figure 3 graphically displays the relaxed positions of the atoms compared with the bulk coordinates. The magnitudes of the in-plane displacements Δx and Δz are generally smaller than the changes in interlayer separation (δd), and decrease with depth. The breaking of mirror-plane symmetry is needed to achieve a fit of this quality, and is qualitatively consistent with the STM and LEED results of Züger and Dürig [13], but not the LEED work of Hofmann *et al.* [16]. To visualize the effect of the model's atomic displacements on nearest-neighbor interatomic distances, Fig. 4 plots bond length vs depth from the surface for the dimer bond (D) and the three metallic bonds ($M1$, $M2$, and $M3$). The trend is a decrease in metallic bond lengths and a slight increase in dimer bond lengths. The differences in bond lengths from bulk values are generally greatest at the surface, decreasing towards the bulk. The $M2$ bond, of which there are two per bilayer, tends to zigzag.

If one assumes that bond *length* is a measure of bond *strength*, then the α -Ga(010) surface is clearly more metallic than the bulk. This enhanced metallicity comes at the expense of the covalent dimer bonds, which are somewhat weakened (lengthened) relative to bulk dimers. This finding is in complete accord with photoemission experiments by Hofmann *et al.* [16], which found a metallic surface state in the $\bar{C}-\bar{X}$ direction of the surface Brillouin zone, for temperatures above 210 K. Bernasconi

TABLE I. In-plane and interlayer displacements from bulk for one domain of our model of α -Ga(010), a relaxation of surface B , with $\chi^2 = 2.43$. Errors, based on a least-squares fit, are in parentheses.

i	Δx_i (\AA)	Δz_i (\AA)	$(\frac{\delta d}{d})_{i,i+1}$ (%)
1	0.0125(36)	0.0084(8)	-9.6 ^a
2	-0.0054(44)	0.0071(7)	10.2 ^b
3	0.0107(27)	0.0014(8)	-0.9 ^a
4	0 ^c	0.0052(7)	0.8 ^b
5	0 ^c	-0.0037(7)	-3.4 ^a

^aWithin one metallic bilayer; $d = 1.472 \text{ \AA}$.

^bBetween metallic bilayers; $d = 2.357 \text{ \AA}$.

^cFixed.

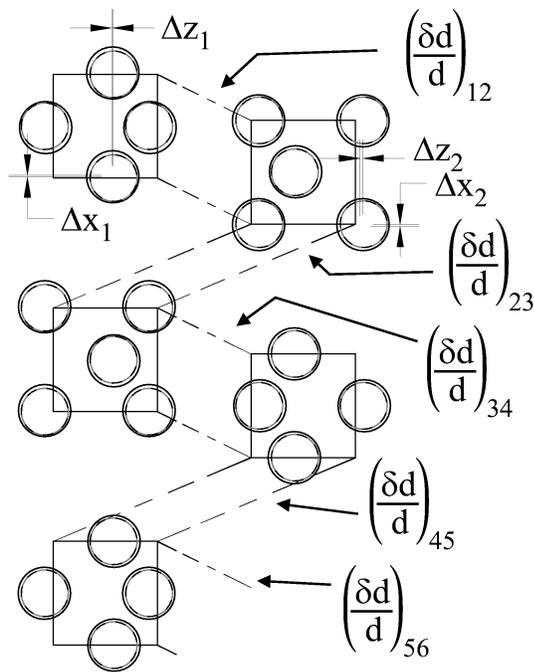


FIG. 3. Layer-by-layer dissection of our model for the α -Ga(010) surface structure. Smaller, broken circles represent bulk atomic positions, while the larger circles represent relaxed positions. Atomic and interlayer displacements are labeled.

et al. [11] predicted α -Ga(010) would be stable as a fully metallic surface, but their proposed surface had a completely different structure.

To conclude, we find using surface x-ray diffraction that the structure of α -Ga(010) is a relaxation of surface *B*, the surface created by cutting through dimer bonds. To our knowledge, this is the lowest-symmetry surface structure determined with x-ray diffraction to date. At the surface, metallic bonds are contracted and covalent dimers

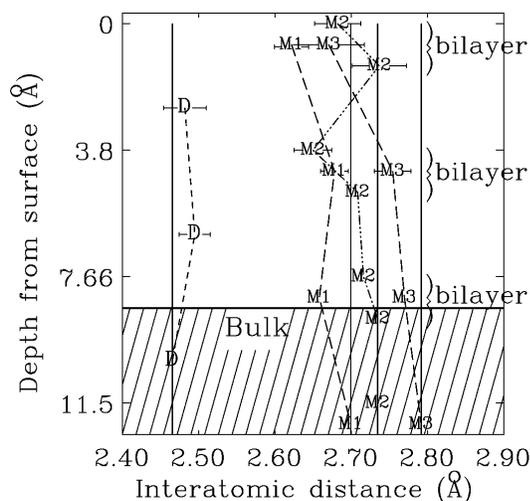


FIG. 4. Nearest-neighbor atom separations classified by bond type (as defined in Fig. 1) versus depth from surface. Error bars are displayed when larger than symbols. Solid vertical lines represent bulk bond lengths; note that all bond lengths in the shaded region were fixed at bulk values.

are expanded. This result is difficult to reconcile with the traditional view of Ga₂ dimers being the building blocks of the bulk α -Ga structure, which should lead to an *A*-terminated surface. It is only reasonable if the fundamental building blocks are the corrugated metallic bilayers as suggested by Häussermann *et al.* [10]. However, this surface still leaves one unsaturated dangling bond per surface atom. These dangling bonds might be satisfied in another α -Ga surface structure, the $c(2 \times 2)$ reconstruction observed with LEED below 210 K by Hofmann *et al.* [16]; this speculation invites a full structural study for this low-temperature phase. We hope further calculations will be performed to confirm the stability and determine the band structure of the high-temperature *B* surface of α -Ga(010). Even the bulk structure of α -Ga is difficult to calculate, since several metastable and high-pressure phases of Ga lie close in energy to the stable α phase. Accurately calculating Ga surface structures would therefore be a stringent test of theoretical methods.

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