The (001) Surface of α-Ga is Covered with Ga III

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We propose, based on *ab initio* calculations, that the ground state (001) surface of α-Ga should be covered by two layers of Ga III, a denser phase which is stable in the bulk only at high pressure and temperature. We discuss how this novel prediction can explain recent scanning tunneling microscopy observations, including anomalous thermal stability of this surface.

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When two or more phases compete for the ground state of a bulk system there is a chance to find strange phenomena at the surface of the lowest energy phase. One such scenario is the formation of a thin film of one of the losing structures at the surface of the winning bulk phase. There are known examples of this behavior. In surface melting when the temperature is still below the bulk melting point, most crystal surfaces "self-wet" with a thin liquid film [1]. Another example is the valence transition at the surface of Sm metal, which has valence 3^+ in the bulk but becomes 2^+ at the surface, in spite of a 0.26 eV/atom cohesive energy difference between bulk Sm^{3+} and Sm^{2+} [2]. These "self-wetting" phenomena can be rationalized on the basis of a common ingredient: the emergent surface phase has a sufficiently lower surface free energy to make it worthwhile paying the film plus interface free energy costs. The physical mechanisms underlying the surface free energy gain of the emergent phase may, however, have very different origin. In the case of surface melting, the surface free energy of the liquid is lower than that of the solid, mostly due to entropy [1]. In metallic Sm the surface energy of the Sm^{2+} state is lower, due to closer similarity to the divalent ground state of the free atom [2]. These surface energy gains are usually quite small, and the closeness of the bulk free energies is thus a necessary condition for the self-wetting to appear.

It is known both experimentally [3] and theoretically [4] that solid Ga presents a rather complicated phase diagram, with many stable and metastable phases closely competing for the ground state. The stable phase at low temperature and ambient pressure is α-Ga, which presents a remarkable coexistence of metallic and covalent character. The energetically closest phases are Ga II [3,5], Ga III [3], and β-Ga [6], which are denser, and fully metallic.

In this Letter, based on accurate *ab initio* total energy calculations, we propose that a thin film of the Ga III phase should cover the (001) surface of α-Ga in its ground state, therefore providing a novel realization of the self-wetting scenario.

The α-Ga lattice is base-centered orthorhombic with eight atoms in the conventional unit cell [7] (inset of Fig. 1). Each atom has one neighbor only in the first coordination cell at 2.44 Å, with six further neighbors within 0.39 Å. The structure can be seen as the stacking along the [001] direction of strongly buckled metallic planes connected by short covalent bonds [4]. The structure of the α-Ga(001) surface has been recently investigated by scanning tunnel microscopy (STM) [8,9], where it appears to be unusually stable: no step diffusion or other type of surface mobility was detected up to the bulk melting point (T_m = 303 K). Even more surprisingly, at T_m the Ga crystal begins to melt from *inside* the sample, with the surface still appearing flat, and atomically ordered [9]. Besides, this surface raises additional questions. In principle, in fact, the ideal α-Ga (001) surface can be formed in two ways, by cutting the crystal at (a) a plane that separates dimer layers, without cutting "covalent" bonds

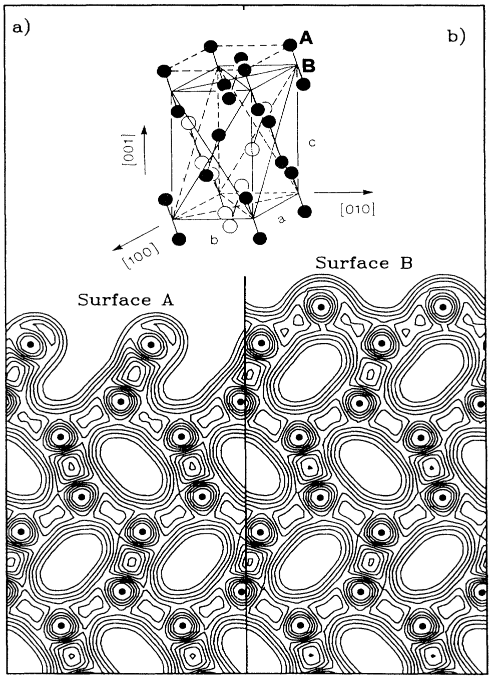

FIG. 1. (a) Charge density of relaxed surface A plotted onto the (100) plane passing through all atoms shown, σ = 57 mRy/atom; (b) same as in (a) for surface B, σ = 57 mRy/atom. Inset: Orthorhombic unit cell of α-Ga [7].

(surface A) [Fig. 1(a)], or at (b) a plane that cuts the dimer covalent bonds (surface B) [Fig. 1(b)]. The top-view geometries for the ideal surfaces A and B are the same, and can be described by a nearly square lattice with two atoms per surface cell, forming chains along the [100] direction, with coordinates (in lattice units) (0,0,0) and (0.5,0.34,0). The STM map, shown in Fig. 2(a), clearly shows this chain structure (a small dimerization of the chain was also inferred [8]). Now, if both configurations A and B were simultaneously realized, for example in adjacent domains, then steps with a height of $c/4 \simeq 1.9$ Å should be present; conversely if one of the two surfaces had a much lower energy, the smallest step height expected is $c/2 \simeq 3.8$ Å. The observed step-height distribution [8] supports the latter scenario, with just a single step of 3.8 Å height. However, this still does not distinguish between possibilities A, B, or others.

We studied both surfaces A and B by means of total energy calculation within the local density approximation [10]. We used first-principle norm conserving pseudopotential of the Kleinman-Bylander form [11]. The surfaces were modeled by periodic slabs, 10 to 14 layers thick, separated by four vacuum layers. Kohn-Sham orbitals were expanded in plane waves up to 14 Ry energy cutoff. Convergency of k sums was tested up to 49 k points in the irreducible ideal surface Brillouin zone (ISBZ); Gaussian spreading with variance from 20 to 5 mRy was used. The lattice parameters were obtained by an independent bulk calculation [12]. Guided by the calculated Hellmann-Feynman forces we let the atoms in the slab relax to their lowest energy positions, with residual forces less than 1.5×10^{-3} Ry/a_0.

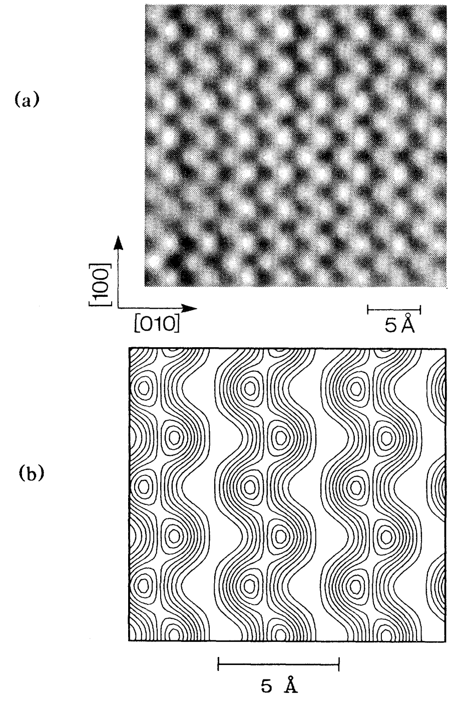

FIG. 2. (a) Experimental STM image of α-Ga(001) [8]. (b) Local density of states $\rho(\mathbf{r}, \Delta E)$ calculated for surface C at a plane $z \simeq 2$ Å above surface atoms, and including states inside an energy window $\Delta E = 0.5$ eV below the Fermi level. In the simplest approximation this plot corresponds to the theoretical STM image with states at the ISBZ boundary playing the major role [18]. States from 36 k points at the boundary of the ISBZ were included. Note the close similarity of features in the two pictures.

Figures 1(a) and 1(b) show the electronic (pseudo) charge density on a (100) plane, for fully relaxed configurations of surfaces A and B, respectively. Surface A has energy $\sigma = 70$ mRy/atom when unrelaxed, and 57 mRy/atom when fully relaxed. For the unrelaxed and relaxed B surfaces we find $\sigma = 59$ and 57 mRy/atom, respectively [13]. Surface energies were obtained by subtracting from the slab total energy the bulk energy for the same number of atoms, calculated with a k point sampling as close as possible to that used in the slab calculation, and are converged within 1 mRy/atom. These values for the surface energies appear to be high when compared with the $T = 0$ K extrapolation of the experimental result $\sigma_{\text{expt}} = 41$ mRy/atom [14]. The two relaxed surfaces A and B end up having the same energy, which does not explain the STM step-height distribution. Moreover, the strong corrugation of charge density in surface A [Fig. 1(a)] looks unreasonable, and indirectly suggests the existence of a different ground state. Also, the chain structure in surface A is different from the STM image. Surface B is instead far more compact, and its chain structure is very similar to the STM image, but it has one unsaturated dangling bond per atom, which again suggests instability. Guided by this reasoning we rearranged drastically surface A, by pushing the outermost atom down to fill the hole underneath. This is equivalent to adsorbing a plane of adatoms onto surface B, therefore removing the dangling bonds. We find a dramatic lowering of σ down to 47 mRy/atom, which now compares much better with the experimental value. In Fig. 2 we compare the STM image calculated for the new optimal surface configuration (hereafter referred to as C) with the experiment [8]. The characteristic chain present in the data is very well reproduced by our model. Also the nonspherical shape of the experimental current spots, with a flat region at one side, compares well with our theoretical image. Our results do not explain the apparent chain dimerization, but this effect probably involves energies below our present resolution.

The charge density of surface C on the (100) plane is plotted in Fig. 3. Remarkably, the structure of the two outermost surface layers and their optimal charge density have become very reminiscent of those of bulk Ga III (inset). Bulk Ga III is a tetragonally distorted fcc structure, stable at high pressure and temperature [3]. The chain structure at surface C is not present in the geometry of Ga III. However, we have checked that, by

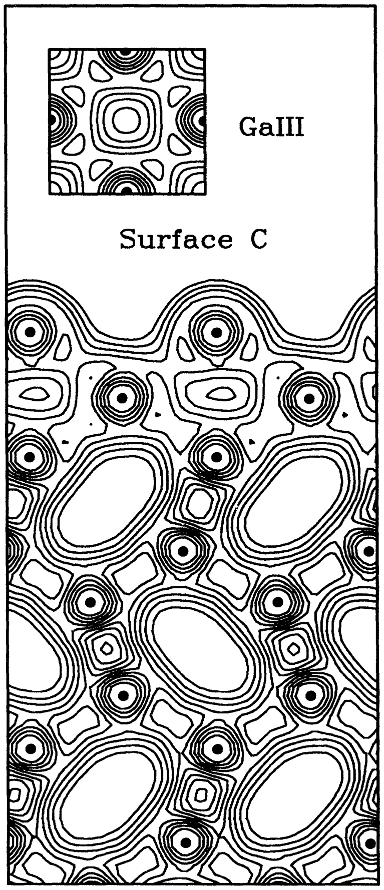

FIG. 3. Charge density for our proposed optimal structure for α-Ga(001) (surface C). $\sigma = 47$ mRy/atom. The fully relaxed interlayer distance for the outermost layers d_{12}, d_{23}, d_{34} are 0.380, 0.347, and 0.525, respectively, in units of $a_0 = 4.377$ Å. The corresponding (x, y) in-plane coordinates (in lattice units) of the two atoms per cell in the four outermost planes are (0,0) (0.5,–0.324); (0,0.505) (0.5,0.171); (0,0.002) (0.5,–0.326); (0,0.179) (0.5,–0.502), respectively. The two outermost surface layers now mimic closely the bulk Ga III phase (inset).

forcing Ga III to have the same *in plane* lattice constants as those of α-Ga, the fcc-like symmetry is unstable and the chain structure appears also in the bulk. This structure mimics Ga III epitaxially grown on α-Ga and will be referred to as "epitaxial Ga III." A separate study (made with a twelve-layer slab) of the free surface of epitaxial Ga III gives rise to a top layer structure which is identical to that of our surface C. We also find that the surface energy of epitaxial Ga III is 43 mRy/atom. This value is sufficiently lower than the surface energy of the ideal configurations ($\sigma_A = \sigma_B = 57$ mRy/atom) to make it worth paying for the α-Ga/(Ga III) interface energy plus the difference in bulk energies of α-Ga and epitaxial Ga III [$\Delta E = E_{\text{bulk}}(\text{epitaxial Ga III})\text{-}E_{\text{bulk}}(\alpha\text{-Ga})$ which we have calculated to be ~ 5 mRy/atom] in the film covering the surface in configuration C. All these results support the prediction that *in the ground state the (001) surface of α-Ga should be wetted by two layers of Ga III epitaxially grown on α-Ga.*

Since by adding a third Ga III layer one produces a step height roughly one half the experimental value, the wetting must be confined to the first two layers up to T_m, in order to be consistent with STM. Indeed, by a separate calculation, we find that the surface energy of the relaxed configuration with *three* layers of Ga III is as high as 60 mRy/atom, similar to σ_B. These values, compared with that of surface C ($\sigma_C = 47$ mRy/atom), guarantee that the configurations with one and two, or with two and three Ga III layers cannot be simultaneously present, in agreement with the observed step height distribution. Furthermore the surface energy for three Ga III layers is much higher than the value obtained by adding to σ_C the energy difference $\Delta E \sim 5$ mRy/atom, required by the added Ga III plane. This suggests a strong attraction between the surface and the α-Ga/(Ga III) interface, which should also exclude the configurations with four or five planes of Ga III (not investigated). Therefore the wetting of α-Ga by epitaxial Ga III is incomplete.

The surface-interface attraction produces a 3D atomic density in the Ga III film roughly 8% higher than the bulk equilibrium density of epitaxial Ga III. If this density increase were obtained by hydrostatic pressure it would cause Ga III to melt about 100 K above the melting temperature of α-Ga [15]. We believe that this explains the anomalous thermal stability of the α-Ga(001) surface detected experimentally [8,9].

We have also calculated the surface stress tensor, which we find to be tensile for surface C: $A^{-1}\,\partial\sigma/\partial\epsilon_{xx} = -29$ mRy/atom and $A^{-1}\,\partial\sigma/\partial\epsilon_{yy} = -20$ mRy/atom. (x and y are the abscissa and the ordinate in Fig. 2, A is the surface area, and ϵ_{ij} is the strain.) This is obviously connected with the lateral expansion required for the structure of Ga III to fit epitaxially on α-Ga, with the associated contraction in the vertical direction.

The presence of the Ga III film induces a large increase in the surface-projected electronic density of states (SDOS) at the Fermi level with respect to the bulk density of states, characterized instead by pronounced pseudogap at E_F [4,16] (details of surface band structure and densities will be discussed elsewhere [16]). Surface B shows a SDOS peak at E_F due to dangling bonds (not present in surface A). The SDOS of surface C is more smooth and metallic, as in epitaxial Ga III. This "metallization" of the surface should show up in photoemission measurements. The Ga III film should induce also detectable modifications in the phonon spectra: the bulk phonon modes around 7 THz [17], associated to the stretching of the dimer covalent bond, should be absent or strongly modified in the surface projected phonon density of states. A more decisive test of our picture should of course come from structural tools, such as ion scattering, dynamical low-energy electron diffraction (LEED), x-ray or atom diffraction, which should be able to discriminate between A, B, and C structures. Static LEED is not sufficient, since the 2D space group is the same for A, B, and C surfaces.

Finally, we may wonder whether this kind of solid-state incomplete wetting is a peculiar feature of α-Ga(001) surface or could be envisaged for other solids too. In general the presence of half-filled dangling bonds makes the surface energy of unreconstructed semiconductors higher than the surface energy of metals with respect to their cohesive energy. If a simple reconstruction, still preserving the "covalent bonding" is not feasible, then the wetting with a fully metallic phase should in principle be favored. This seems to be the case for the α-Ga(001), where the plausible structure of the ideal surface (B) does retain covalent unsaturated dangling bonds. Two other circumstances make the transformation possible on α-Ga(001), namely the closeness in energy between α-Ga and "epitaxial" Ga III, as well as a strong interface attraction which appears to limit the wetting film thickness to strictly two atomic layers.

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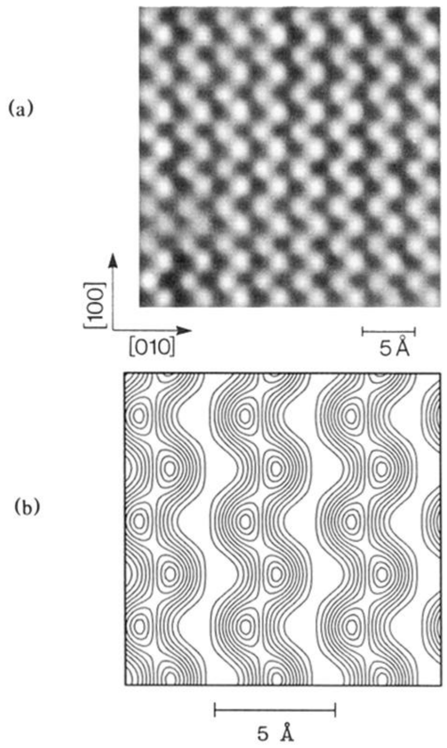

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