

Anomalous Bismuth-Stabilized (2×1) Reconstructions on GaAs(100) and InP(100) Surfaces

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First-principles phase diagrams of bismuth-stabilized GaAs- and InP(100) surfaces demonstrate for the first time the presence of anomalous (2×1) reconstructions, which disobey the common electron counting principle. Combining these theoretical results with our scanning-tunneling-microscopy and photoemission measurements, we identify novel (2×1) surface structures, which are composed of symmetric Bi-Bi and asymmetric mixed Bi-As and Bi-P dimers, and find that they are stabilized by stress relief and pseudogap formation.

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A prerequisite for understanding several phenomena taking place on semiconductor substrates, such as chemical reactions, epitaxial growth, and self-assembly of nanostructures, is the knowledge of atomic structures of adsorbate-stabilized semiconductor surfaces. The common principles for these surfaces are as follows: (a) removal of the dangling bonds, (b) stress relief of the surface layer, and (c) tendency to a semiconducting rather than metallic band structure [1]. A modification of the last principle is the well-known electron counting model (ECM) for compound semiconductors [1–11]. Based on ECM, the surface energy is reduced when all dangling bonds of the electropositive atoms (e.g., group-III), which lie above the Fermi energy, become empty of electrons and those of the electronegative atoms (e.g., group-V), which lie below it, become doubly occupied.

For III-V(100) semiconductor surfaces, which several technologies such as wireless and optical communications are based on, the ECM principle predicts a semiconducting reconstruction with vacant dimer sites. This means that part of paired surface atoms is missing, and the (2×4) or (4×2) unit cells are the smallest ones on V- and III-stabilized III-V(100) surfaces. Although, in general, the observed reconstructions agree well with ECM, there are indications for anomalous surfaces [7,12–15]. The semiconducting P-stabilized (2×1) reconstruction on InP(100) is one of the most interesting examples [12]. Such a small unit, however, should include a half-filled dangling bond,

and thus the (2×1) surface without any dimer vacancies should be metallic and unstable. Nevertheless, later this P/InP-(2×1) has been shown to be stabilized by hydrogen adsorbate [13].

Thus, the recent finding that a group-V adsorbate (Bi) induces well-ordered (2×1) reconstructions on various III-V(100) surfaces is challenging [16–18]. In general, understanding the properties of these Bi/III-V-(2×1) surfaces is crucial to determine the detailed physical mechanisms of III-V reconstructions and the epitaxial growth of III-V materials for electronics, the latter being essentially a surface process proceeding via V-stabilized

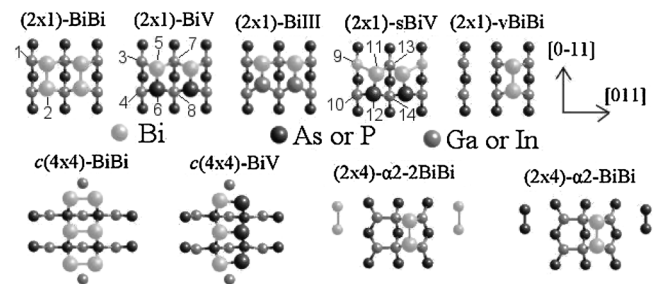


FIG. 1. Atomic models for Bi-induced (2×1), (2×4), and $c(4 \times 4)$ reconstructions on GaAs and InP. Bi coverages are 1, 0.5, 0.5, 0.75, and 0.5 ML for BiBi, BiV, BiIII, sBiV, and vBiBi, respectively, and 0.75, 0.375, 0.5, and 0.25 ML for $c(4 \times 4)$ -BiBi, -BiV, (2×4)- $\alpha 2$ -2BiBi, and -BiBi. The numbered atoms are used to describe bond lengths in Table I.

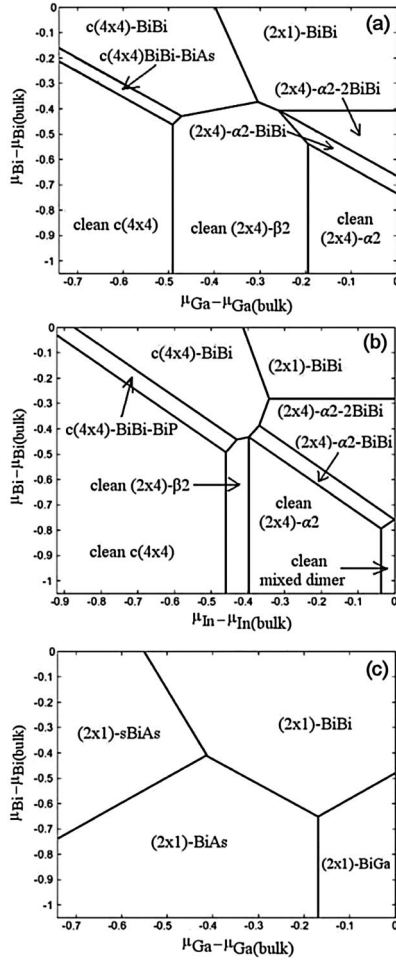


FIG. 2. Phase diagrams for Bi/GaAs (a) and Bi/InP (b). Relative stabilities of (2×1) structures on Bi/GaAs (c). For Bi/InP, the (2×1) diagram is similar to Fig. 2(c), but the BiGa is replaced by the ν BiBi.

reconstructions. In particular, Bi has been utilized as surfactant in the growth [18–21] and also alloyed with III-V's (e.g., $\text{GaAs}_{1-x}\text{Bi}_x$) to produce spintronics materials [22]. To realize why the Bi surfactant on the growing surface changes the characteristics of device materials (e.g., leads to smoother interfaces and higher photoluminescence intensity [20,21]), it is of great importance to understand the fundamental properties of the Bi/III-V surfaces.

The previous scanning-tunneling-microscopy (STM) study of Bi/III-V- (2×1) [17,18] could not resolve many important properties (e.g., chemical composition and atomic geometry) and mysteries related to this anomalous surface. In this Letter, we address this problem by combin-

ing first-principles calculations with photoemission and STM measurements. Here, we present the first theoretical phase diagrams for Bi/III-V and for the energetically favored (2×1) structures, and by comparing our measured and calculated photoemission and STM data, identify hitherto not reported (2×1) structures. We also shed light on the fundamental questions of why both semiconducting and metallic Bi/III-V- (2×1) form and what their stabilizing mechanisms are.

The measurements were done at room temperature in ultrahigh vacuum (UHV). STM images were taken in the constant current mode. Photoelectron spectroscopy was done at MAX-lab (BL 41) in Sweden. The GaAs(100) substrate was grown by molecular beam epitaxy (MBE) and transferred under UHV into the photoemission chamber. Another MBE-grown GaAs with a protective As cap against air exposure was used for STM. These substrates were heated at 570 °C until (6×6) low-energy-electron-diffraction (LEED) patterns were seen. A 1–1.5 monolayer (ML) of Bi was deposited on them. When the Bi/GaAs was heated at 270 °C (4 hours), clear (2×1) LEED without any other phase was seen. Above 300 °C, LEED showed a combined pattern of (2×1) and (2×4) .

The theoretical calculations were performed using the *ab initio* DFT total-energy code with the local density approximation [23,24]. The approach is based on plane wave basis and projector augmented wave method [25,26] (Vienna *ab initio* simulation package, VASP) [27]. The (2×1) reconstructions (Fig. 1) were simulated with (2×2) slabs including 13 atomic layers and treating the Ga 3*d* electrons as valence electrons. The relative stabilities of (2×1) , (2×4) , and $c(4 \times 4)$ were calculated using (4×4) slabs with 9–10 atomic layers and keeping all *d* electrons in the core. Pseudohydrogenated slabs were used [28] with the cutoff of 280 eV. The number of *k* points in the Brillouin zone was 9 and 4 for (2×2) and (4×4) slabs, respectively. The surface energies were evaluated as a function of chemical potentials (μ) in the standard way. Core-level shifts (CLS) were calculated within the initial state model [28] and ascertained by the DMOL3 program [29].

The theoretical phase diagrams for Bi/GaAs and Bi/InP [Figs. 2(a) and 2(b)] demonstrate the stability of the (2×1) reconstructions. Calculations also indicate that the Bi-stabilized (2×4) - $\alpha 2$ reconstructions appear when the Bi amount decreases. Indeed, the $\alpha 2$ phases are found in experiments only after heating the (2×1) surfaces to desorb Bi partly [16–18]. According to Figs. 2(a) and 2(b), the (2×4) - $\beta 2$ structure, being stable on several

TABLE I. Calculated bond lengths (*d* in Å) between atoms labeled with numbers in Fig. 1 for BiBi, BiV, and sBiV structures. Bucklings of Bi-V dimers, *b*(BiV) and *b*(sBiV), are also shown.

<i>d</i>	2–2	1–2	5–6	3–5	4–6	5–7	6–8	11–12	9–11	10–12	11–13	12–14	<i>b</i> (BiV)	<i>b</i> (sBiV)
Bi/GaAs	3.02	2.78	2.82	2.82	2.45	2.70	2.45	2.71	3.17	2.45	2.82	2.44	0.39	0.50
Bi/InP	2.97	2.92	2.56	3.02	2.56	3.02	2.56	2.58	3.40	2.55	3.00	2.53	0.42	0.50

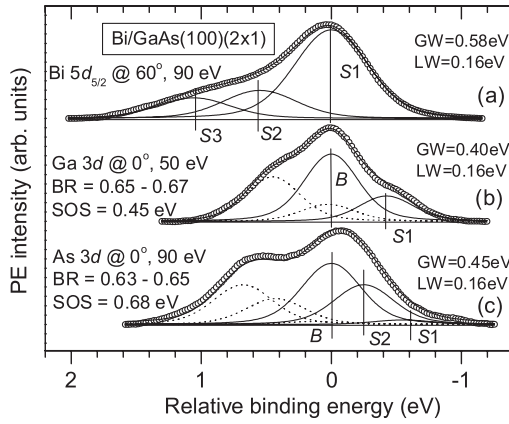


FIG. 3. Fitted Bi $5d_{5/2}$ (a), Ga $3d$ (b), and As $3d$ (c) core-level spectra from Bi/GaAs- (2×1) . Emission angle from the surface normal and photon energy are shown for each spectrum. Also, Gaussian width (GW), Lorentzian width (LW), spin-orbit splitting (SOS), and branching ratio (BR) are shown. Solid lines show $d_{5/2}$ peaks of the doublets.

III-V surfaces, is not stabilized by Bi. This finding agrees well with the present and former STM measurements [16–18], in which $\beta 2$ has not been observed. The Bi/III-V- $c(4 \times 4)$ structures, seen in the upper left corner of Figs. 2(a) and 2(b), were not found in our measurements. This may be attributed to the fact that in experiments, the III-rich substrates were used for Bi deposition.

Theory shows that only one type of the (2×1) structure is stable [Figs. 2(a) and 2(b)]. This is composed of symmetric Bi-Bi dimers (labeled as BiBi in Fig. 1). On the other hand, the reconstructions formed can be affected by surface kinetics [1], which depend on the surface preparation, and are not taken into account in the above thermodynamic diagrams. Therefore, here we also consider other possible (2×1) phases. The diagram of the most favored phases is shown in Fig. 2(c). Schematic plots (with selected bond lengths) for these phases are given in Fig. 1 (Table I). Surprisingly, calculations show that the mixed Bi-As and Bi-P dimers are buckled about 0.4–0.5 Å (Table I). This is in contrast with previous findings for group-V dimers [1,6,7,10], and it is supported below by the comparison of our measured and calculated STM images. Regarding the electric conductivity, our calculated electronic struc-

tures (not shown) indicate that BiBi, vBiBi, BiGa, BiAs, and BiP are metallic, as expected, and sBiAs and sBiP are semiconducting with the energy gap of about 0.5 eV. This is reasonable because the number of available electrons in sBiAs and sBiP is exactly the same as needed to fill all the bonds. In the following, by comparing the calculated and measured core-level and STM results, we identify those phases that explain the observed Bi/III-V- (2×1) reconstruction.

Core-level spectra of Bi/GaAs- (2×1) are shown in Fig. 3 and their CLS are listed in Table II together with the calculated CLS. With our experimental resolution (0.2–0.3 eV), the comparison of the calculated and measured CLS shows that a dominant area of Bi/GaAs- (2×1) can be described with either BiBi, BiAs, or BiGa or with their combination. Also, local sBiAs domains are proposed to exist and cause the Bi $5d$ S2 and S3 emissions. The presence of several (2×1) phases, which is supported by our STM observations below, causes a variation in the Bi $5d$ energy (Table II), and is the most likely reason for the broadened peaks. The atomic origins of Bi S1, S2, and S3 are, respectively, the dimer (in BiBi, BiAs, or BiGa), the dimer of sBiAs, and the second-layer Bi of sBiAs. The Ga S1 arises from the second layer, As S1 from the third layer, and As S2 from the dimer of sBiAs.

The STM image of Bi/GaAs- (2×1) is shown in Fig. 4(a). Its comparison with the calculated images in Figs. 4(e)–4(h) demonstrates the existence of symmetric Bi-Bi dimers. Furthermore, valence-band photoemission (not shown) reveals a substantial emission at the Fermi energy, supporting the presence of metallic areas on Bi/GaAs- (2×1) . [Our valence-band measurements reveal metallic areas also on Bi/InP- (2×1) , agreeing with the STM results in the next paragraph.] Indeed, the $I(V)$ curve and its differential [Fig. 4(b)], obtained for the same region as Fig. 4(a), show the metallic character of the Bi/GaAs- (2×1) area. These findings confirm that the BiBi areas appear on Bi/GaAs- (2×1) , in good agreement with our total-energy results [Fig. 2(a)]. The STM image of the high-temperature surface [Fig. 4(c)], including both (2×1) and (2×4) phases, suggests the existence of another (2×1) phase(s), which agrees with the calculated BiAs [Fig. 4(g)] and sBiAs [Fig. 4(h)] images. We cannot distinguish between them because of the limited resolution in Fig. 4(c). However, the $I(V)$ curve and its differential

TABLE II. Measured and calculated (by VASP *ab initio* code) core-level shifts (CLS in eV) for Bi/GaAs- (2×1) . Negative values indicate smaller binding energy (BE) as compared to the reference, which is bulk BE for As $3d$ and Ga $3d$. For calculated Bi CLS, 0-eV level is BE in the BiBi structure. In measured Bi $5d$, S1 is set at 0 eV. Calculated shifts smaller than 0.1 eV are not listed.

Bi/GaAs- (2×1)	Bi $5d$	Ga $3d$	As $3d$
Measured CLS	0(S1), +0.55(S2), +1.06(S3)	−0.42(S1)	−0.55(S1), −0.25(S2)
VASP: BiBi	0	−0.31, −0.16	−0.25
VASP: BiGa	−0.14	−0.35, −0.26, −0.13	−0.10
VASP: BiAs	+0.23	−0.35, −0.18	−0.37, −0.23
VASP: sBiAs	+0.35, +0.88	−0.43, −0.36, −0.12	−0.49, −0.20, +0.12, +0.25

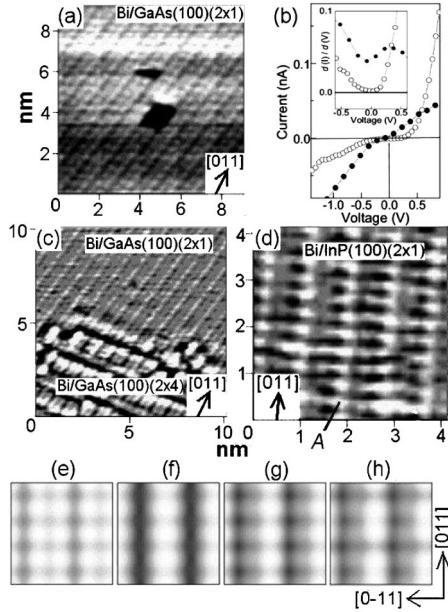


FIG. 4. (a) Filled-state STM image of Bi/GaAs-(2×1); tunneling current $I = 0.09$ nA and voltage $V = 1.70$ V. (b) $I(V)$ curves are averages of the well-ordered areas on Bi/GaAs-(2×1); solid and open symbols are from the areas similar to Figs. 4(a) and 4(c), respectively; inset shows corresponding differential curves. (c) Filled-state STM image of Bi/GaAs, which consists of both (2×1) and (2×4) phases; $I = 0.42$ nA and $V = 2.49$ V. (d) Filled-state STM image of Bi/InP-(2×1) from Ref. [17]; $I = 0.51$ nA and $V = 1.73$ V. (e)–(h) Calculated filled-state STM images for Bi/GaAs-(2×1)-BiBi (e), -BiGa (f), -BiAs (g), and -sBiAs (h) with the voltage of 1.7 V.

[Fig. 4(b)] from the high-temperature (2×1) phase indicate semiconducting sBiAs. Its presence is also supported by our photoemission findings (Table II).

A third structure is found on InP: the calculated BiP image (BiP is metallic), similar to the BiAs image in Fig. 4(g), describes the best our STM image for Bi/InP-(2×1) [Fig. 4(d)] [17]. This allows us now to identify the white protrusion A from Fig. 4(d) as an upper Bi atom of the buckled Bi-P dimer. The previous results [17] suggest also the appearance of semiconducting sBiP areas.

To answer the question of why the Bi/III-V-(2×1) structures are stable, we recall that their stability was intuitively proposed [17] to be due to surface stress relief. The present results provide clear evidence for that. Although the stresses do not vary significantly between Bi/GaAs-(2×1)-BiBi and various (2×4) and hypothetical (2×1)-AsAs and (2×1)-SbSb structures, the stress relief due to the relaxation of the adsorbate atom is found to be the largest on (2×1)-BiBi. For example, the dimerization decreases the surface stress by 105.3, 50.0, and 41.1 meV/Å² on (2×1)-BiBi, -SbSb, and -AsAs, respectively. Upon dimerization, the change in the dimer bond length is found to be largest, and therefore, to a large

extent, the above changes in the surface stress may be attributed to the stress relief experienced by the dimers. The largest relief on (2×1)-BiBi describes the fact that Bi atoms have the largest tendency to dimerize. This is because Bi atoms have a strong attractive interaction on the (1×1) atomic positions as a result of their large size. We conclude that the above mechanism is the main driving force behind Bi/GaAs-(2×1)-BiBi. Another stabilizing factor appears in the calculated density of states (DOS, not shown): DOS near the Fermi energy is lower on (2×1)-BiBi than on (2×1)-AsAs and -SbSb; i.e., a pseudogap forms on (2×1)-BiBi. [A certain number of states still appears at the Fermi energy on (2×1)-BiBi, agreeing with the metallic character found above.] The pseudogap may also be associated with the Bi size. The Bi-Ga backbond is long, resulting in larger p_z occupation compared to p_x and p_y occupations in contrast to (2×1)-AsAs. Consequently, the sp_3 hybridization changes to the p_3 hybridization, which is also revealed in the angles between backbonds (90.39°). Thus, this hybridization leads to the opening of the pseudogap at the Fermi energy.

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