Dimensional crossover and chirality of boron adsorbates on copper (110) surfaces

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A copper boride phase found on Cu(110) exhibits dimensional crossover from 1D to 2D structures. The discovered surface phase, $7 \times '1'$ -B/Cu(110), is composed of alternating two-atom and three-atom rows that are separated by trenches. The narrower rows behave as a 1D template for atomic boron chains, and the wider rows provide a new dimensional degree of freedom that facilitates the generation of 2D clusters with chirality. The $7 \times '1'$ phase is nonperiodic in the chain direction and exhibits intermediate boron coverage, between that of the quasiperiodic 1D and periodic 2D phases of copper boride on Cu(110), demonstrating a unique feature of phase transitions at the surface.

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I. INTRODUCTION

Polymorphism is one of the central issues related to the structure in materials science [1] and has been described based on mathematical methods, such as topology, which have also been applied to various fields of research. For example, topology is related to neural networks in the body and the configurations in computing [2]. Notably, boron is known to form various polymorphs owing to the unique chemical properties of the multicenter bonding scheme [3]. Numerous boron structures have been reported for different allotropes and compounds. Focusing on the dimensionality in metal borides, the boron networks in the 3D (bulk) crystal have been empirically identified depending on a ratio, R = x/y, of the chemical stoichiometry, $M_x B_y$, where M is the metal element. Boron configurations in 3D metal compounds include 0D atoms ($R \ge 3$), 1D chains ($R \sim 1$), 2D layers ($R \sim 1/2$), 3D structures ($R \sim 1/4$), and octahedron clusters ($R \sim 1/6$) [4-6]. Recently, there has been growing interest in boron adsorbates on crystal surfaces. Surfaces are inherently twodimensional and serve as convenient systems for investigating boron polymorphism in low dimensions (i.e., 0D, 1D, and 2D), such as atomic sheets of boron, *borophene* [7–9], and 2D metal borides [10,11].

Regarding the surfaces of copper crystals, borophene preferentially forms on Cu(100) [12], whereas 2D copper boride forms on Cu(111) with an alternating array of zigzag 1D chains comprising copper and boron atoms [13,14]. Note that copper and boron atoms do not form copper borides in 3D structures, and the boride formation at the surface is due to the unique properties of materials in low dimensions. Recently, there have been reports on various surface phases of characteristic 1D structures, formed on Cu(110) [15,16]. At the initial stage of boron growth, diffraction and microscope experiments observed the $3 \times$ '1'-B/Cu(110) phase [15,17]. On the surface, atomic boron chains are fragmentarily formed with quasiperiodicity along the 1D direction and the surface is well described by the structure model, based on symmetric two-atom copper rows. At the different boron coverage, microscopy research found the formation of the $7 \times$ '3'-B/Cu(110) phase that is composed of metalloborophene nanoribbons [16]. Boron adsorbates on the standard crystal surfaces of copper have now become significant playgrounds for investigating the nature of boron polymorphs, especially for examining their dimensionality.

In the present research, an ordered phase, namely $7 \times$ '1', was observed by scanning tunneling microscopy (STM) after depositing boron on Cu(110). The phase exhibited intermediate boron coverage, consisting of the 3×1 phase [15,17] and the $7 \times 3^{\circ}$ phase [16]. The $7 \times 1^{\circ}$ structure is composed of trenches that are regularly arranged with alternating threefold $(3\times)$ and fourfold $(4\times)$ periodicities. The STM appearance of the $3 \times 1^{\circ}$ part is similar to the previously reported quasiperiodic 1D structure [15,17]. The $4 \times$ '1' part exhibits a nonperiodic structure with various local structures, including chiral structures that contain pairs of enantiomers. Based on the atomic chain model for the $3 \times 1^{\circ}$ phase, the chiral structures can be described in terms of 2D boron clusters with triangular and linear components, and the optimized structure models were determined by performing first-principles calculations. The results demonstrate the dimensional crossover of the boron polymorphs from 1D to 2D in the copper boride layer on the Cu(110) surface.

II. EXPERIMENTAL

Sample surfaces were prepared on commercial Cu(110) crystals (Matech, Germany). First, the surfaces were cleaned by Ar^+ sputtering at 0.5 kV and annealing at 600 °C. The cleanliness was confirmed by STM and low-energy electron diffraction (LEED). The B/Cu(110) surfaces were obtained by depositing boron (99.999% pure) on the clean Cu(110)

substrate at 500 °C, as previously reported [14,15,17,18]. The nominal boron coverage, regulated by the deposition time, was three times higher than that of the $3 \times 1^{-B}/Cu(110)$ surface, reported previously [15].

STM images were obtained using a commercial STM instrument (Omicron, Germany) with a Nanonis SPM control system. Topographic imaging was performed at 80 K (liquid N₂) using a tungsten tip in constant current (I_t) mode at various sample biases (V_s) [15]. The image analysis was conducted using WSxM [19] and Gwyddion [20] software. All the surface preparation and STM imaging procedures were performed under ultrahigh vacuum with a base pressure below 1.0×10^{-10} Torr.

Theoretical calculations were conducted to further examine the boron structures on Cu(110), based on optimization of the total energy. All the calculations were performed using Quantum ESPRESSO v.7.1, which is a firstprinciples code derived from density functional theory and the planewave and pseudopotential methods [21-23], with the effective screening medium method (vacuum/slab/vacuum boundary condition) [24]. Perdew–Burke–Emzerhof ultrasoftpseudopotentials were taken from a standard solid-state pseudopotentials library and employed in the calculations for efficiency (SSSP-efficiency v.1.1.2) [25,26]. The cutoff energies for the wave function and the charge density were set to 90 and 720 Ry, respectively. For the optimizations, the convergence criteria for the total energy and the force were set to 1.0×10^{-4} Ry and 1.0×10^{-3} Ry/Bohr, respectively. We modeled the slab as five atomic layers of Cu(110), followed by the adsorbate atom clusters (N = 3) depicted in Fig. 4 and a vacuum layer. The vacuum layer was 20 Å or more. The Monkhorst–Pack k-point sampling [27] was $3 \times 3 \times 1$, with orthorhombic lattice parameters of a = 15.18, b = 14.31, and c = 27.0Å.

III. RESULTS AND DISCUSSION

A. STM observation on the 7 × '1' phase

Figure 1(a) shows STM images of the surface after depositing boron on the Cu(110) crystal at 500 °C. In addition to the known $7 \times 3^{\circ}$ phase [16], a new phase, $7 \times 1^{\circ}$, was observed. The $7 \times 1^{\circ}$ phase was developed systematically after adsorbing boron on Cu(110) for three times longer deposition time than the condition for the $3 \times 1^{\circ}$ phase reported previously [15]. This fact leads to the estimation of the nominal boron coverage in the present case for the $7 \times 1^{\circ}$ phase. In the previous STM experiment [15], 20% of the surface was covered with the $3 \times 1^{\circ}$ phase that has a chemical stoichiometry of Cu:B=1: 1.57, as determined by XPS [17]. Combing this information, one can evaluate ~ 0.6 ML of boron coverage for the present growth condition, where 1 ML corresponds to the surface atomic density of Cu(110). It is of note that our STM observation found an area of the pristine Cu(110) surface and, thus, it likely requires boron deposition of > 0.6 ML to cover the entire surface. Focusing on the detailed features of the surface phases, the $7 \times 3^{\circ}$ phase appears as nanoribbons with regular trenches of \sim 2.42 nm interval that forms a sevenfold periodicity of the Cu(110) lattice along the [001] axis [16]. The $7 \times 1^{\circ}$ phase also has the sevenfold



FIG. 1. STM images of 1D structures grown by boron deposition on Cu(110). (a) Mixed phases of $7 \times '3'$ and $7 \times '1'$ -B/Cu(110) and (b) a single phase of $7 \times '1'$ -B/Cu(110). The 1D phases in (a) are labeled as $7 \times '1'$ and $7 \times '3'$, but the $7 \times '1'$ phase in (b) is further classified into the 1D regions, $4 \times '1'$ and $3 \times '1'$. The high symmetry directions of a Cu crystal and a scale bar are given in the figure. The STM conditions are outlined as follows: (a) $I_t = 104 \text{ pA}$, $V_s = 1.5 \text{ V}$; (b) $I_t = 104 \text{ pA}$, $V_s = 1.5 \text{ V}$.

periodicity but it contains trenches of alternating rows of the fourfold (4×) and the threefold (3×) intervals, as shown in Fig. 1(b). The observed lengths of the 4× and 3× periodicities correspond to 1.02 ± 0.06 nm and 1.41 ± 0.05 nm, respectively.

Boron deposition on Cu(110) results in various phases, including 3×1^{2} , 7×1^{2} , and 7×3^{2} -B/Cu(110). The 7×3^{2} phase does not completely cover the B/Cu(110) surface shown in Fig. 1, but the boron coverage is higher than that of the previously reported 3×1^{2} -B phase [15]. Thus, the 7×1^{2} phase provides intermediate boron coverage, between that of the other two phases, 7×3^{2} and 3×1^{2} . It has been reported that the 3×1^{2} -B/Cu(110) surface is composed of aligned 1D quasi-periodic structures [15]. Thus, a 1D 7×1^{2} phase likely contains a combination of quasiperiodic 1D



FIG. 2. STM images of the 7 × '1' phase. (a) A filled-state STM image obtained using $I_t = 104$ pA and $V_s = 1.5$ V. The high symmetry directions of a Cu crystal and a scale bar are given in the figure. (b)–(e) Images of local structures in the 4 × '1' region.

 $(3 \times '1')$ and periodic 2D $(7 \times '3')$ copper boride structures on Cu(110).

Figure 2 (a) shows a closer STM image of the $7 \times 1^{\circ}$ phase. The sevenfold periodicity $(7 \times)$ is observed along the [001] crystal axis. In contrast, no apparent periodicity is observed in the perpendicular direction, the $[1\overline{1}0]$ axis, and thus the surface phase is named $7 \times 1^{\circ}$. Furthermore, the $7 \times 1^{\circ}$ phase is composed of alternating $3 \times 1^{\circ}$ and $4 \times 1^{\circ}$ units that are aligned in parallel. The $3 \times 1^{\circ}$ unit contains a trench and two types of symmetric protrusions along the 1D direction that generate the quasiperiodicity, as previously reported [15]. The $4 \times 1^{\prime}$ unit contains a trench and a wider 1D structure compared with that of the $3 \times 1^{\circ}$ unit. On the structure, four types of bright features are observed, as depicted in Fig. 2(b)-2(e), which can be further classified into two groups of enantiomers. Namely, the features in Figs. 2(b) and 2(c) are mirror images of each other, and the same relationship is observed in Figs. 2(d) and 2(e).

Figure 3(a) and 3(b) provides a collection of STM line profiles taken from the corresponding regions in the image of the $7 \times 1^{\circ}$ surface. The distributions of the relative heights along the 1D direction are similar (< 10 pm) for the $3 \times 1^{\circ}$ and $4 \times 1^{\prime}$ units. Along the perpendicular direction, deep trenches with similar depth profiles are observed between the units. An interval of the peaks (valleys) in intensity profiles along the [001] axis (line 4) was evaluated 0.35 ± 0.03 nm $(0.32 \pm 0.02 \text{ nm})$, which commensurately matches with the lattice constant of the Cu(110) crystal along the direction. This fact indicates that the peak in profiles or the bright protrusion in images is assigned to a Cu atom, and the surface structure can be described by the Cu row model. In addition, $3 \times 1^{\circ}$ and $4 \times 1^{\circ}$ share the same microscopic features, as shown in Fig. 3(c). Between the brighter regions in each unit, pairs of oval structures were found in the dark regions, with different groupings or numbers of pairs: 1 [Figs. 3(d) and 3(e)], 2 [Figs. 3(f) and 3(g)], or 3 [Figs. 3(h) and 3(i)]. The microscopic appearance of the $3 \times 1^{\circ}$ unit was identical to that of the $3 \times$ '1'-B/Cu(110) phase [15], comparing the STM images taken with the opposing sample biases of 1.5 V [filled-state image, Fig. 2(a) and -1.5 V [empty-state image, Fig. 3(a)]. Thus, the $3 \times 1^{\circ}$ unit can be described using the structure



FIG. 3. Empty-state STM images taken at $I_t = 104 \text{ pA}$ and $V_s = -1.5 \text{ V}$. (a), (b) The line profiles are taken along the directions indicated in the STM image, from the regions marked by rectangles. The profiles in (b) are obtained along the long side of the rectangles labeled in (a), after individually integrating along the short side. The 4 × '1' and 3 × '1' units are indicated with red and blue bars, respectively. (c) The enlarged image of the 7 × '1' phase. (d)-(i) A collection of the oval pair structures observed in the (d), (f), and (h) 3 × '1' and (e), (g), and (i) 4 × '1' units in (c), with a blank added after (h) and (i). The high symmetry directions of a Cu crystal and a scale bar are given in the figure.

model previously reported for the $3 \times '1'$ -B/Cu(110) surface [15]. Moreover, the similarity of the structure in the $3 \times '1'$ unit with that in the $3 \times '1'$ model allows us to infer the $4 \times '1'$ structure by comparison.

STM images show that the $3 \times 1^{-B}/Cu(110)$ surface contains trenches and two types of symmetric protrusions along the 1D direction that generate the quasiperiodicity [15]. First-principles calculations revealed that the $3 \times 1^{\circ}$ structure is composed of a symmetric two-atom Cu row and incommensurate boron chains [15]. Surface reconstruction at the Cu(110) surface induces the two-atom Cu rows, providing a 1D template for boron adsorbates. The bright regions in the STM image are attributed to the boron adsorbates and the dark regions are attributed to the bare Cu rows. Based on the 3×1 '-B structure model, the 4×1 ' structure can be deduced. Specifically, the $4 \times 1^{\circ}$ unit is composed of a three-atom Cu row and boron adsorbates. Moreover, boron adatoms have more freedom in 2D on the $4 \times 1^{\circ}$ unit than in 1D on the 3×1 unit, owing to the wider template. This allows for the attachment of a boron atom to the side of the boron chain, forming a 2D structure composed of boron clusters. This is in contrast to the 1D template of $3 \times 1^{\circ}$, where an additional atom can only bond at a terminal end of the boron chain. The Cu row model is consistent with the identical STM features observed in the dark regions in Figs. 3(c)-3(i), which are assigned to the bare Cu row. These findings indicate that the surface structure of the 7×1^{-B} phase comprises



FIG. 4. Polymorphs of the boron structures formed on a 1D anisotropic substrate. (a)–(j) The original figures and the mirror images, symmetrically operated by the mirror plane, (M_{yz}) : (a) twoatom chain, (b), (c) comblike three-atom chain, (d), (e) trimer, (f) three-atom chain, (g), (h) comblike four-atom chain, and (i), (j) trimer with chain. (k), (l) Structure models of (k) the *B*₄-cluster chain [16] and (l) *cis-bumulene* [14]. The number of atoms (*N*) and the first-order Betti number (b_1) are shown for the individual models. The existence of enantiomers and the mirror plane symmetry, $\chi(M_{zx})$, are indicated for the corresponding models.

alternating arrays of three-atom and two-atom Cu rows with incommensurate 1D and 2D boron adsorbates, respectively.

B. A boron trimer model on the copper row

Although STM has become widely adopted to examine surface structures at the atomic scale, it is not possible to accurately determine the arrangement of atoms from complex and nonuniform STM images alone. Nonetheless, the $3 \times 1^{\prime}$ unit in the $7 \times 1^{\prime}$ -B phase appears to be similar to the $3 \times 1^{\prime}$ -B phase that was reported to have an atomic boron chain structure [15]. Thus, as a first step, it is possible to design a precursor of the 2D structure that induces the chirality in the $4 \times 1^{\prime}$ unit by adding an atom to the boron chain model in the $3 \times 1^{\prime}$ -B phase or $3 \times 1^{\prime}$ unit.

Figure 4 summarizes the various boron polymorphs that may form on a 1D anisotropic surface containing two-atom and three-atom chains along the x direction, with the addition of an atom connected from the new dimension (y direction). The models are classified by the number of atoms (N), the first-order Betti number (b_1) [28], the existence of mirror images (enantiomorphs) with respect to the M_{yz} plane, and the mirror symmetry with the M_{zx} plane, $\chi(M_{zx})$. The Betti number is adopted here since the quantity has been used in algebraic topology to distinguish shapes of the target. In the context of the graph theory, b_1 is defined for a graph G with n vertices, m edges, and k connected components as m - n + k. In brief, the b_1 value is referred to as the number of holes. Figure 4(a) illustrates a linear biatomic cluster $(N = 2, b_1 = 0)$. An additional atom can be attached at one side of the atom (N = 3), Fig. 4(b), along the y-direction or the other (N = 3), Fig. 4(c), keeping $b_1 = 0$. These structures individually constitute the enantiomers with respect to the M_{yz} plane. When another atom bonds with the two atoms, the cluster becomes a trimer ($N = 3, b_1 = 1$). Whereas the trimer structure of Fig. 4(d) is achiral with M_{yz} , the trimer structure of Fig. 4(e) is chiral with M_{yz} after rotation. In the case of adding an atom to a linear triatomic cluster ($N = 3, b_1 = 0$), Fig. 4(f), an attachment (N = 4) at the edge leads to the generation of chirality and the formation of enantiomorphs, Fig. 4(g), whereas attachment at the center becomes achiral with M_{yz} , Fig. 4(h). In the N = 4 cluster, a triangular bonding configuration $(b_1 = 1)$ can partially form, as shown in Figs. 4(i) and 4(j). For both cases, the structures have enantiomers. For comparison, Figs. 4(k) and 4(l) shows structure models that were previously reported for boron adsorption layers on Cu crystal surfaces [14,16]. The model of a B_4 -cluster chain [16] is adopted as a component of the metalloborophene nanoribbons on Cu(110), and that of *cis-bumulene* [14] is discussed as a unit of a periodic array of boron chains on Cu(111). These structures contain linear and triangular parts, as considered in Figs. 4(a)-4(j). The universality in the formation of boron trimers and their connections is consistent with the structures observed for 2D clusters and borophene [3].

Considering the combination of boron adsorbates and the reconstructed Cu(110) surface, we then focus on the mirror symmetry $\chi(M_{zx})$ that exists in the copper row model and some of the boron polymorphs listed in Fig. 4. The condition is satisfied for the trimer model, Fig. 4(e), and the linear-trimer model Fig. 4(j), suggesting that these adsorbate structures are favorable. Note that the symmetry $\chi(M_{zx})$ holds in this model, Fig. 4(a) and 4(f), as proposed for the $3 \times '1'$ -B/Cu(110) phase [15], and in a 1D component in the B_4 -cluster model [16], Fig. 4(k), as proposed for $7 \times '3'$ - B/Cu(110).

To investigate the atomic arrangement of the boron adsorbate on the Cu(110) surface, first-principles calculations were conducted for the N = 3 boron cluster. Among the possible models given in Figs. 4(b)–4(e), the trimer model was found to be the most stable on the Cu row, as shown in Fig. 5. The comblike models (N = 3, $b_1 = 0$) in Figs. 4(b) and 4(c) become the trimer (N = 3, $b_1 = 1$) in Fig. 4(e) after structure optimization, with energy difference of -35 meV/atom. The orientation of the trimer in Fig. 4(e) was much more favorable on the Cu row than the other one in Fig. 4(d), as expected from the discussion on M_{zx} symmetry.

An optimized structure of the trimer model elucidates further details of the surface reconstruction. From the top view, Fig. 5(a), the boron trimer appears as a triangle, whereas the oblique and side views, Fig. 5(b) and 5(c), reveal that one of the boron atoms is located lower than the other two and the neighboring copper atoms shift outward compared with the bare Cu row atoms. Figure 5(d) shows a set of the optimized trimer model with its mirror image, symmetrically operated by the mirror plane (M_{yz}). Notably, the chirality of the boron trimer induces the chirality in the Cu row. Thus, the local structures are the enantiomers that likely grow in size from the addition of more boron atoms. These results indicate that the local structures of the 4×'1' unit are associated with unique arrangements of copper and boron atoms.

While further efforts are needed to determine the precise surface structures that reproduce the experimental STM images, the micrographs of the boron adsorbates on the Cu rows describe the dimensional evolution, providing clues for the appropriate structure model. Considering the similarities in the boron network and the symmetry, the cluster structure of the trimer model, Fig. 4(e), appears to be related to precursors of the B_4 -clusters or *bumulene* that were



FIG. 5. Optimized atomic structure of the N = 3 boron polymorph on the reconstructed $4 \times '1'$ -B/Cu(110) unit, obtained by first-principles calculation. The model is shown from the (a) top, (b) oblique, and (c) side views with indications of the high symmetry directions of a Cu crystal. (d) The structure model and its mirror image. Boron atoms and the neighboring copper atoms are colored in red. A dotted line in the middle represents the mirror plane (M_{yz}) defined in Fig. 4.

experimentally observed on the B/Cu surfaces in a previous report [14,16].

C. STM observation of a single atomic row

The present research on the B/Cu(110) system reveals a significant role of the surface reconstruction in Cu rows. During boron deposition, the two-atom and three-atom rows tend to induce the $3 \times 1^{\circ}$ and $4 \times 1^{\circ}$ units, respectively. Thus, it is expected single-atom Cu rows also form on the B/Cu(110) surface, as shown in Fig. 6(a). Figure 6(b) provides an STM image of the boundary between the bare Cu and $3 \times 1^{\circ}$ -B



FIG. 6. An STM image of the edge of the $3\times$ '1' phase. (a) Atomic model of a reconstructed Cu(110) surface with Cu rows: (i) a single-atom Cu row and (ii) a two-atom Cu row. (b) The STM image, using $I_t = 104$ pA and $V_s = -1.20$ V. The scale bar is indicated in the figure.

domains on Cu(110). The width of the 1D feature at the edge is as narrow, approximately half the width of the 1D protrusion in the $3 \times 1^{\prime}$ domain, which consists of two-atom Cu rows. It appears that the single-atom Cu row exists at the domain boundary, consistent with the copper row model adopted for the $7 \times 1^{\prime}$ phase. For the B/Cu(111) phase, the surface structure is composed of alternating arrays of atomic boron and copper chains [13,14,18]. At the Cu surface, there may be a unique relationship between the atomic Cu chain and the boron adatom, which may be revealed through further research.

IV. CONCLUSION

An ordered copper boride phase, $7 \times 1^{\circ}$, was found on Cu(110) by STM, exhibiting intermediate boron coverage between that of the $3 \times 1^{\circ}$ phase [15,17] and the $7 \times 3^{\circ}$ phase [16]. The $7 \times 1^{\circ}$ structure is composed of alternating $3 \times 1^{\circ}$ and $4 \times 1^{\circ}$ units that are aligned in parallel. The $3 \times 1^{\circ}$ part is similar to the previously reported quasiperiodic structure of the $3 \times 1^{\circ}$ phase [15], whereas the $4 \times 1^{\circ}$ part is disordered along the 1D direction. The $4 \times 1^{\circ}$ part comprises pairs of mirror-imaged structures, indicating the existence of the enantiomers. Through topological classification, 2D boron cluster models have been discussed with the aid of first-principles calculations. The present results help clarify the transformation of boron polymorphs into higher dimensional structures on Cu surfaces.

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APPENDIX: STM SIMULATION OF THE Cu ROW MODEL WITH A BORON CLUSTER

The constant-current scanning tunneling microscopy (STM) simulations were performed based on the Tersoff-Hamann approximation implemented in Quantum ESPRESSO [29]. For the constant-current STM calculations, we employed a *k*-point sampling of $4 \times 4 \times 1$ and a sample bias of -1.5 and 1.5 V (the calculations take the states in the energy window below the Fermi energy, from $\varepsilon_F + V$ to ε_F , V = -1.5, 1.5). The value of the charge of the isosurface was set to 5×10^{-5} . The search space of the isosurface is between 5.4 and 21.6 Å in the *z* direction, which encompasses the Boron cluster.

Figure 7 presents simulation results of the Cu row model (a),(b) with or (c),(d) without the boron trimer at different biases. In all the images, one can clearly identify atomic trenches in the model as the dark 1D structure. At $V_s = -1.5$ V, the fine features of the Cu atoms can be seen in the row and, in addition, the boron trimer is found as a protrusion. At $V_s = 1.5$ V, Fig. 7(b) displays that the Cu and B atoms



FIG. 7. STM simulations of the three-atom copper row model with a boron trimer cluster. Calculated images are obtained at sample bias, V_s , of (a) -1.5 and (b) 1.5 V. The structure model and the simulated image are given on the left and right sides, respectively. In between the two sides, the figures are overlapped with each other at different ratios of transparency for comparison. A result of the pristine Cu row model is also given for V_s of (c) -1.5 and (d) 1.5 V as a reference.

have rather uniform contrast but the surrounding of the boron cluster appears differently, showing the moatlike dark feature. Although the simulation was held on the precursor model with a single cluster, the appearance was consistently found in STM images of the actual surface, shown in Figs. 1 and 3. Atomlike protrusions are found in the experimental image at $V_{\rm s} = -1.5$ V, while unique dark features are observed lo-

- A. J. Cruz-Cabeza, S. M. Reutzel-Edens, and J. Bernstein, Chem. Soc. Rev. 44, 8619 (2015).
- [2] T. Martinetz and K. Schulten, Neural Networks 7, 507 (1994).
- [3] I. Matsuda and K. Wu (eds.), 2D Boron: Boraphene, Borophene, Boronene (Springer International Publishing, Cham, 2021).
- [4] T. Lundström, *Encyclopedia of Inorganic and Bioinorganic Chemistry* (John Wiley & Sons, Ltd, 2011).
- [5] G. Akopov, M. T. Yeung, and R. B. Kaner, Adv. Mater. 29, 1604506 (2017).
- [6] K. Izumi and K. Kudaka, The Academic Reports, the Faculty of Engineering, Tokyo Polytechnic University, 21 (1998), https: //kougei.repo.nii.ac.jp/records/309.
- [7] Z.-Q. Wang, T.-Y. Lü, H.-Q. Wang, Y. P. Feng, and J.-C. Zheng, Front. Phys. 14, 33403 (2019).
- [8] B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, and K. Wu, Nat. Chem. 8, 563 (2016).
- [9] A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, and N. P. Guisinger, Science 350, 1513 (2015).
- [10] F. J. Tuli, G. Peng, S. Hossain, K. Ninomiya, R. Ahmed, T. Nakagawa, and S. Mizuno, Surf. Sci. 713, 121906 (2021).

cally at $V_s = 1.5$ V. Comparisons of these images unveil the significance of the boron adsorbates to change the appearance of Cu rows in STM. Although it requires much effort in both experiments and calculations for structural analysis, the present results on the model likely provide an important perspective in determining the accurate structure of the B/Cu(110) surface phase.

- [11] X.-J. Weng, X.-L. He, J.-Y. Hou, C.-M. Hao, X. Dong, G. Gao, Y. Tian, B. Xu, and X.-F. Zhou, Phys. Rev. Mater. 4, 074010 (2020).
- [12] R. Wu, S. Eltinge, I. K. Drozdov, A. Gozar, P. Zahl, J. T. Sadowski, S. Ismail-Beigi, and I. Božović, Nat. Chem. 14, 377 (2022).
- [13] C. Yue, X.-J. Weng, G. Gao, A. R. Oganov, X. Dong, X. Shao, X. Wang, J. Sun, B. Xu, H.-T. Wang, X.-F. Zhou, and Y. Tian, Fundamental Res. 1, 482 (2021).
- [14] Y. Tsujikawa, M. Horio, X. Zhang, T. Senoo, T. Nakashima, Y. Ando, T. Ozaki, I. Mochizuki, K. Wada, T. Hyodo, T. Iimori, F. Komori, T. Kondo, and I. Matsuda, Phys. Rev. B 106, 205406 (2022).
- [15] Y. Tsujikawa, X. Zhang, K. Yamaguchi, M. Haze, T. Nakashima, A. Varadwaj, Y. Sato, M. Horio, Y. Hasegawa, F. Komori, M. Oshikawa, M. Kotsugi, Y. Ando, T. Kondo, and I. Matsuda, Nano Lett. 24, 1160 (2024).
- [16] X.-J. Weng, Y. Zhu, Y. Xu, J. Bai, Z. Zhang, B. Xu, X.-F. Zhou, and Y. Tian, Adv. Funct. Mater. 34, 2314576 (2024).
- [17] Y. Tsujikawa, X. Zhang, M. Horio, T. Wada, M. Miyamoto, T. Sumi, F. Komori, T. Kondo, and I. Matsuda, Surf. Sci. 732, 122282 (2023).

- [18] Y. Tsujikawa, X. Zhang, M. Horio, F. Komori, T. Nakashima, Y. Ando, T. Kondo, and I. Matsuda, J. Surf. Sci. Nanotechnol. 22, 1 (2024).
- [19] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, Rev. Sci. Instrum. 78, 013705 (2007).
- [20] D. Nečas and P. Klapetek, Central Eur. J. Phys. 10, 181 (2012).
- [21] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).
- [22] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [23] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
- [24] M. Otani and O. Sugino, Phys. Rev. B 73, 115407 (2006).
- [25] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [26] G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet, and N. Marzari, npj Comput. Mater. 4, 72 (2018).
- [27] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- [28] W. Lück, in *Geometric and Cohomological Methods in Group Theory*, London Mathematical Society Lecture Note Series, edited by I. J. Leary, M. R. Bridson, and P. H. Kropholler (Cambridge University Press, Cambridge, 2009), pp. 63–161.
- [29] J. Tersoff and D. R. Hamann, Phys. Rev. B 31, 805 (1985).