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Structure and growth of Bi(110) islands on Si(111)$\sqrt{3}\times\sqrt{3}$-B substrates

Kentaro Nagase,[1] Ikuya Kokubo,[2] Shiro Yamazaki,[1] Kan Nakatsuji,[2] and Hiroyuki Hirayama[1,*]

[1]*Department of Physics, Tokyo Institute of Technology, J1-3, 4259 Nagatsuda, Midori-ku, Yokohama 226-8502, Japan*
[2]*Department of Materials Science and Engineering, Tokyo Institute of Technology, J1-3, 4259 Nagatsuda, Midori-ku, Yokohama 226-8502, Japan*

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The structure and growth of ultrathin Bi(110) islands were investigated on a Si(111)$\sqrt{3}\times\sqrt{3}$-B substrate by scanning tunneling microscopy and scanning tunneling spectroscopy (STS). Both even- and odd-layer-height islands nucleated on a one-monolayer-thick wetting layer. The islands preferred the even layer heights over the odd layer heights with an area ratio of 3:1. A weak, long-range corrugation was observed to overlap on the atomic arrangement at the top of the islands. The average distance between the peaks of the corrugation oscillated in accordance with the alternation of even and odd layer heights. Nucleation of single- and double-layer terraces occurred on the islands with even layer heights but not on those with odd layer heights. The unit cell of the single-layer terrace was aligned with that of the underlying even-layer-height island. The inequality in the height preference and the height-dependent oscillation of the corrugation suggested that the even- and odd-layer-height islands possessed different structures. The dominance and stability against terrace nucleation of the even-layer-height islands were consistent with the theoretically predicted stability of the paired layer-stacked black-phosphorus (BP)-like structure for ultrathin Bi(110) films. The alignment of the unit cell at the terrace on the island and STS spectra suggested a BP-like/bulklike/BP-like sandwich structure for the odd-layer-height Bi(110) islands.

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I. INTRODUCTION

Ultrathin Bi(110) films with a black phosphorus (BP)-like allotrope structure are of great interest as candidates for two-dimensional topological insulators [1]. The crystal structure of such films is depicted as a ball-and-stick model in Fig. 1(a). For the purposes of this study, one monolayer (ML) is defined as indicated in Fig. 1. The Bi atoms in each layer are slightly buckled, and two monolayers are paired and stacked along the (110) orientation. These pairs of layers, which we refer to herein as paired layers, are the fundamental building blocks of the BP-like crystal structure. One- and two-paired-layer-thick Bi(110) films were recently predicted to be two-dimensional topological insulators, contingent on realizing the BP-like allotrope structure [1]. Experimentally, ultrathin Bi(110) islands can be nucleated on substrates such as Si(111)7×7 [2–5], $\sqrt{3}\times\sqrt{3}$-B [6], β-$\sqrt{3}\times\sqrt{3}$-Bi [7,8], Ge(111)$c(2\times8)$ [9], W(110) [10], and highly oriented pyrolytic graphite [11,12]. The Bi(110) islands had only even layer thicknesses on the Si(111)7×7 substrate [2]. The exclusive preference for the even layer thickness was attributed to the specific stacking of paired layer units of the BP-like Bi allotrope crystal structure [Fig. 1(a)]. Theoretical calculations also indicated the stability of the BP-like structure compared with the bulklike rhombohedral (A7) structure [Fig. 1(b)] for ultrathin Bi(110) films [2,13]. However, Bi(110) islands with even and odd layer heights were observed to nucleate on Si(111)$\sqrt{3}\times\sqrt{3}$-B, β-$\sqrt{3}\times\sqrt{3}$-Bi, and Ge(111)$c(2\times8)$ substrates [6,7,9]. The BP-like Bi(110) islands cannot form with an odd layer height, whereas the bulklike islands form with even and odd layer heights [14]. In usual cases, it is unlikely that the islands change the crystalline structure depending on the height during the growth. Thus, the Bi(110) islands are implicitly supposed to form a bulklike structure in the growth in those systems [7–9,11]. However, the structure, nucleation, and growth have not been addressed in detail in systems where even- and odd-layer-height Bi(110) islands coexist. In this study, we investigated the growth and structure of ultrathin Bi(110) islands on a Si(111)$\sqrt{3}\times\sqrt{3}$-B substrate by scanning tunneling microscopy (STM) and spectroscopy (STS).

II. EXPERIMENTS

Experiments were carried out in an ultrahigh-vacuum apparatus with a Bi Knudsen cell and a low-temperature STM [15]. Highly B doped Si(111) samples were flashed at 1523 K for 25 s and kept at 1223 and 1173 K for 30 min each. Defect-free Si(111)$\sqrt{3}\times\sqrt{3}$-B substrates were prepared after cooling to room temperature slowly. Bi atoms were deposited on the substrate at a rate of 0.035 ML/min at room temperature. For this study, 1 ML was defined as the density of Bi atoms in a bulklike Bi(110) plane (9.27×10^{14} atoms/cm^2). The height and surface atomic arrangements of the Bi islands were characterized by STM at room temperature and liquid-N$_2$ temperature. STS spectra were acquired by applying a small voltage modulation (25 meV, 1088 Hz) and using the conventional lock-in technique at liquid-N$_2$ temperature.

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[*] hirayama.h.aa@m.titech.ac.jp

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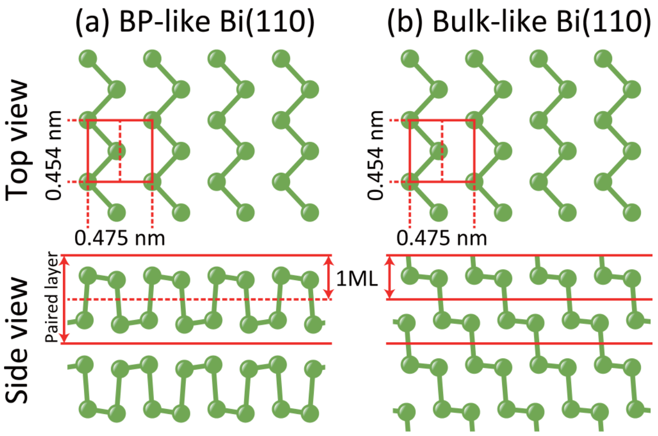

FIG. 1. Ball-and-stick models of the top and side views of the (a) BP-like and (b) bulklike (rhombohedral; A7) crystal structure of the Bi(110) island. The surface atoms form a rectangular unit cell (solid red lines) with a slightly off center atom with respect to the center line (dashed red lines) in both structures. For the purposes of this study, a monolayer (ML) and paired layer are defined as indicated for the BP- and bulklike Bi(110) islands.

III. RESULTS AND DISCUSSION

A. Overview of the growth process of Bi(110) islands and the preference for even layer heights

Figure 2(a) shows an STM image of the Bi islands on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate after depositing 5.6 ML of Bi atoms. The Bi atoms were arranged periodically with a 0.45×0.47 nm^2 off-center rectangular unit cell on the islands, as shown in the inset. This atomic arrangement is the same as that on the BP-like and bulklike Bi(110) surfaces [top views in Figs. 1(a) and 1(b)]. Thus, the islands were unambiguously identified as Bi(110) islands. However, whether they had a BP-like or bulklike structure could not be determined from the atomic arrangement in the STM images.

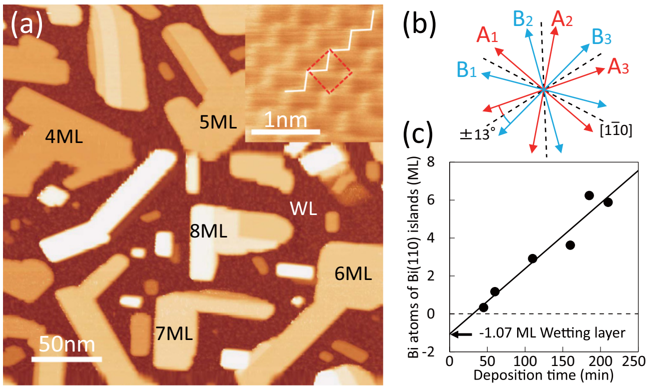

FIG. 2. (a) STM image of Bi(110) islands on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrates after 5.6-ML Bi deposition at room temperature. The heights of the islands on the wetting layer are indicated for some islands. Image size is 270×270 nm. $V_s = +2.0$ V. $I_t = 0.1$ nA. Inset: lattice image of a Bi(110) island. Image size is 2×2 nm. $V_s = -0.6$ V. $I_t = 0.3$ nA. The unit cell and zigzag chain are indicated by a red rectangle and white lines, respectively. (b) In-plane orientation of the islands. The Bi(110) islands extended in one of the six preferred orientations ±13° from the $\lfloor 1\bar{1}0 \rfloor$ direction of the Si(111)1×1 substrate lattice ($A_1, B_1, A_2, B_2, A_3, B_3$). (c) The number of Bi atoms in the islands versus deposition time. The number of Bi atoms is evaluated in units of ML.

The Bi(110) islands extended along six orientations ±13° from the Si(111) $\lfloor 1\bar{1}0 \rfloor$ axes [Fig. 2(b)] because the diagonals of the Bi(110) and Si(111)$\sqrt{3} \times \sqrt{3}$ unit cells were commensurate [6]. However, the gaps between the islands were filled with a wetting layer with dark contrast. This means that the growth proceeded via the Stranski-Krastanov mode [16]. The Bi(110) islands are considered to nucleate on the wetting layer. The heights of the Bi(110) islands were measured from the surface of the wetting layer in the gaps by STM. Figure 2(c) shows the relation between the number of Bi atoms present in the islands and the deposition time. The number of Bi atoms in the islands was evaluated in units of ML by summing the product of the area and height (in units of ML) of each island in the STM images. The intercept of the horizontal axis indicates that the wetting layer had a thickness of 1 ML. The atomic arrangement in the wetting layer was aperiodic in the gaps between the islands (not shown). No periodicity was detected in the fast Fourier transform. However, the islands extended along the commensurate orientations. Thus, we speculate that the wetting layer recovers the Bi(110) periodicity under the islands. The crystallization of the wetting layer has been experimentally verified under Ag(111) islands on Si(111)7×7 substrates in x-ray diffraction studies [17,18]. The growth of the Bi(110) islands along the commensurate orientations could be reasonably explained if the wetting layer crystallized under the islands, as in the case of the Ag islands on the Si(111)7×7 substrate.

The Bi(110) islands were stable even at a height of 20 ML in the growth on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate. No transition to the Bi(111) islands was observed, unlike on the Si(111)7×7 substrate [2]. In the present system, the islands had both even and odd layer heights on the wetting layer [Fig. 2(a)]. For several Bi coverages between 1.6 and 7.3 ML, the distributions of the Bi(110) island height are shown by the histograms in Fig. 3. Each histogram was constructed by analyzing the area of the islands of various heights in more than ten STM images 270×270 nm^2 in size. Figure 3 indicates that the even-layer-height islands (red bars) were always dominant over the odd-layer-height islands (blue bars) in the distributions. The area ratio of even- to odd-layer-height islands was evaluated as ~3 : 1. The height of the islands was found to concentrate on 6, 7, and 8 ML in the histogram for the Bi coverage of 5.6 ML. A similar concentration of the height of the islands was observed at other Bi coverages. The height of the islands concentrated in a region ~3 ML wide in the distribution at each coverage. The distribution shifted toward the larger side with increasing coverage, although the even layer heights remained dominant.

At the top of the Bi(110) islands, weak, long-range corrugations were observed to overlap on the atomic arrangement of Bi atoms for both the even and odd layer heights, as shown in Fig. 4(a). A similar long-range corrugation was observed at the surface of Pb films on Si(111), and a numerical simulation revealed that the corrugation on the Pb island originated from the strain at the interface [19]. Consequently, we speculate that the corrugation originated from the strain at the interface between the Bi(110) island and

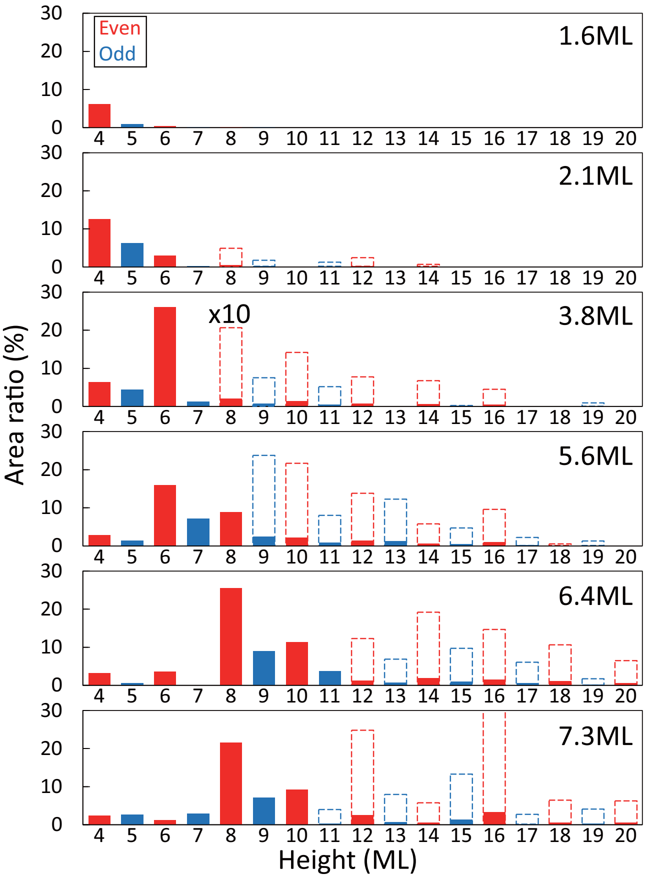

FIG. 3. Height distribution of Bi(110) islands on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate. The heights were measured from the wetting layer. The Bi coverages were 1.6, 2.1, 3.8, 5.6, 6.4, and 7.3 ML. The red and blue bars represent the even and odd layer heights, respectively. For clarity, the distributions at larger heights were magnified tenfold, as indicated by the dashed bars.

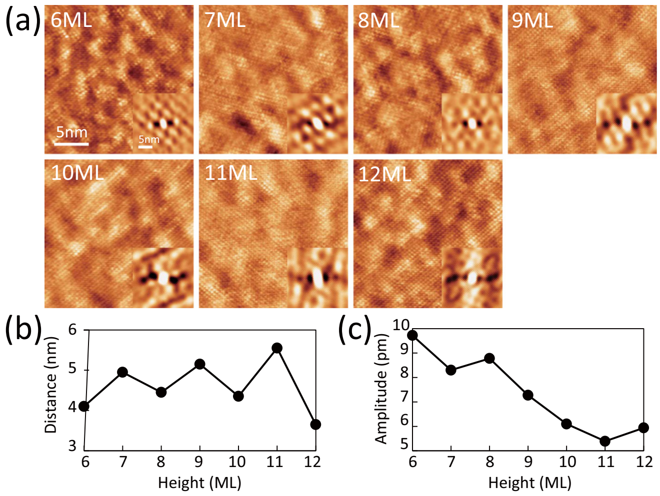

FIG. 4. Long-range corrugation on the Bi(110) islands. (a) STM images of the corrugation. $V_s = -0.5$ V, $I_t = 0.3$ nA. The height of the island is indicated in the top left corner of each image, and the autocorrelation of each image is displayed in the inset. (b) and (c) Height dependences of the average peak distance and amplitude of the corrugation.

the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate, which propagated to the top of the island and caused the corrugation. The peaks in the corrugation seemed to be approximately regularly distributed with a characteristic distance in each STM image. We evaluated the interpeak distance by averaging the distance between the center and the first nearest spots in the autocorrelation of the STM image. The autocorrelation images are displayed in the insets in Fig. 4(a). The amplitude of the corrugation was also evaluated as the root-mean-square value in the STM image. The average peak distance and amplitude of the corrugation are shown as a function of the island height in Figs. 4(b) and 4(c). The amplitude of the corrugation decreased with the thickness of the islands. This observation is consistent with the interface-strain-induced corrugation scenario because the strain is expected to relax with increasing island height. In particular, the interface-strain-induced corrugation was shown to be transferred to the upper layers while decreasing the amplitude in the numerical simulation [19]. The peak distance in the corrugation was greater on the odd-layer-height islands than on the even-layer-height islands [Fig. 4(b)]. The distance oscillated in accordance with the alternation of the odd-even layer heights. This indicates that the in-plane strain was relaxed in different ways in the even- and odd-layer-height islands, suggesting that the even- and odd-layer-height Bi(110) islands possessed distinct structures. Specifically, the Bi(110) island was considered to have a BP- or bulklike structure in previous studies [2,7–9,11]. We found no data for the elastic properties of Bi with the BP- or bulklike structure. However, in the case of nitrogen, which is in the same group of the periodic table as Bi, the bulk modulus was reported to be 1.5 times greater in the BP-like structure than in the bulklike structure [20]. Therefore, it is probable that the BP- and bulklike Bi possess different bulk moduli and exhibit interface-strain-induced corrugations with different peak distances.

B. Nucleation of single- and double-layer-height terraces on even-layer-height Bi(110) islands

Single- and double-layer terraces were frequently observed to nucleate on islands with even layer heights in the growth phase. Representative STM images of the nucleation of 1- and 2-ML terraces on 6-ML-high Bi(110) islands are shown in Figs. 5(a) and 5(b), respectively. In contrast, the nucleation of terraces was never observed on the odd-layer-height islands. Bi atoms must be deposited on the even- and odd-layer-height islands. However, additional layers were always absent on the odd-layer-height islands. This may be due to the instability of the odd-layer-height islands to the nucleation of the overlayers. Specifically, the 1-ML-thick overlayer nucleation triggered the decomposition of the $(2n+1)$-ML-thick odd-layer-height island terrace into the $(2n+2)$-ML-high terrace and $2n$-ML-high island areas. This decomposition explains the absence of terrace nucleation on the odd-layer-height islands and the appearance of the double-layer terraces on the even-layer-height islands. It would also lead to the concentration of the heights in the central 3-ML-wide region, in which a minor odd-layer-height region was sandwiched between two major even-layer-height regions.

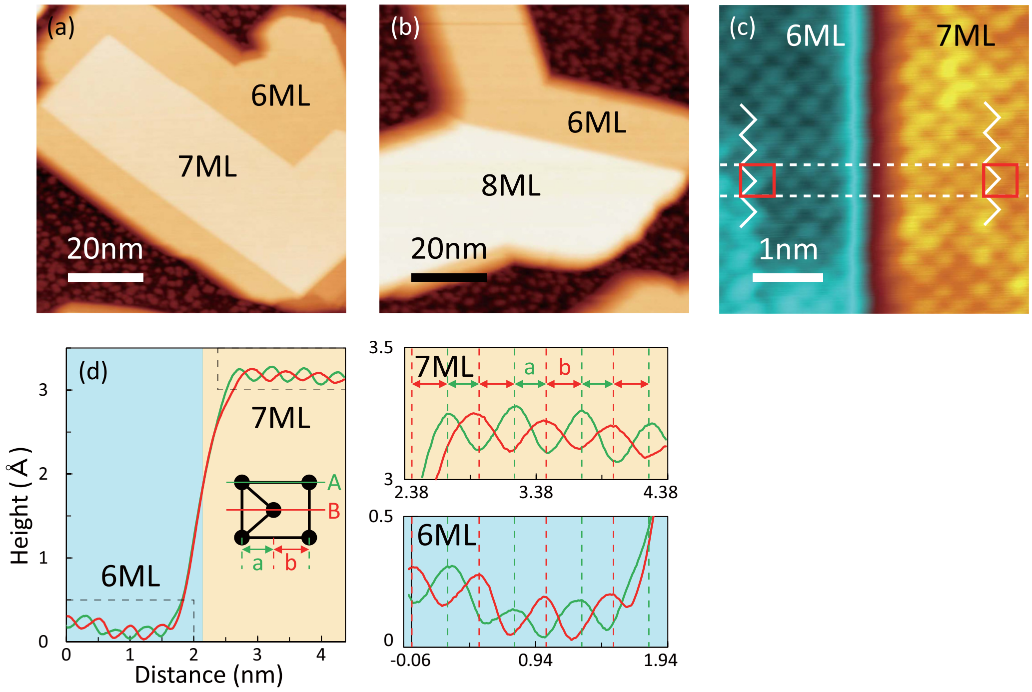

FIG. 5. STM images of (a) single- and (b) double-layer terraces on 6-ML-high Bi(110) islands. $V_s = -2.0\,\mathrm{V}$, $I_t = 0.1\,\mathrm{nA}$. The heights from the wetting layer are shown for the terraces and the islands. (c) Atomically resolved STM image at the edge of the single-layer terrace (7 ML in height) on a 6-ML-high Bi(110) island. $V_s = -0.3\,\mathrm{V}$, $I_t = 1.0\,\mathrm{nA}$. (d) Cross sections of the STM image along lines A (green) and B (red) in the unit cell depicted in the inset. The results from the 7- and 6-ML-high areas are magnified and displayed in the right-hand panels. The cross section was averaged along the direction parallel to the step edge and is displayed.

The dominance and stability of the even-layer-height Bi(110) islands were attributed to the BP-like structure [2,13]. The energetically unfavorable dangling bonds were removed from the surface by making the interlayer bonding in the paired layer in the BP-like structure. Thus, the BP-like structure is more stable than the bulklike structure with unsaturated surface dangling bonds for ultrathin Bi(110) islands, as reported theoretically [2,13]. The BP-like structure with the paired layer stacking can be realized only in the even-layer-height islands. Therefore, the even-layer-height islands are considered to adopt the BP-like structure in the present system.

However, the BP-like Bi(110) islands did not take the odd layer heights. If we try to understand both the even and odd layer heights in terms of a bulklike structure, then the islands are able to have both even and odd layer heights. However, the atomically resolved STM images [Fig. 5(c)] reveal that this cannot be the case in the growth on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate. The off-center Bi atom was bound to the corner atoms on the near side in the unit cell, forming a zigzag chain [inset in Fig. 5(d)]. Thus, the distance from the off-center atom to the edge atoms in the same zigzag chain (i.e., on the near side) must be shorter than that to the edge atoms on the far side, as indicated by a and b in the projection parallel to lines A and B. Furthermore, the zigzag chains tended to be brighter in the STM images. Using these criteria, we identified the positions of the zigzag chains and the unit cells on the single-layer terrace and the 6-ML-high island area [Fig. 5(c)]. The result indicated that the unit cell on the terrace and 6-ML-high area were aligned on the island. However, the zigzag chain in the top layer was displaced by half of a unit cell in plane to that in the second layer in the bulklike structure [Figs. 1(b) and 6(a)]. Thus, the unit cell should be displaced between the two regions if both the 6- and 7-ML-high areas have the bulklike structure [Fig. 6(a)], in contrast to the result in Fig. 5(c). In this respect, the 6-ML-high island with the 7-ML-high terrace did *not* adopt the bulklike structure entirely.

C. A possible structure of the odd-layer-height Bi(110) islands

The single-layer terrace on the 6-ML-high Bi(110) islands could not be explained by either the BP-like or the bulklike structure alone. However, the single-layer terrace could nucleate on the stable BP-like 6-ML-high Bi(110) island if the BP-like structure were to locally change to the bulklike structure just under the terrace region, as illustrated in Fig. 6(b). Bi atoms have been theoretically shown to be capable of flexibly switching between BP-like and bulklike bonding depending on the change in the even-odd parity of the thickness in ultrathin Bi(110) films [13]. However, in this case, energetically unfavorable dangling bonds would be exposed at the surface of the single-layer terrace region. Furthermore, this model is not consistent with the alignment of the unit cells since the zigzag chain on the terrace is displaced relative to that on the 6-ML-high Bi(110) island region by the bonding of the bulklike structure between the top and second layers in the terrace region, as shown in Fig. 6(b). Thus, this structure is also unlikely in the present system.

Recently, a Bi(110)-like single-layer allotrope was observed to nucleate on the even-layer-height Bi(110) islands on the graphite substrate [23]. The Bi atoms arranged with the off-

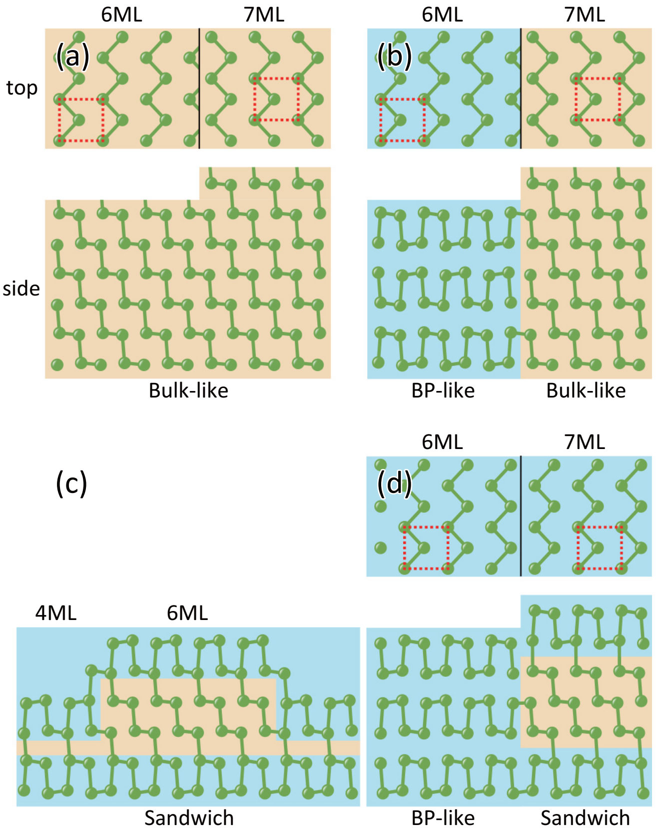

FIG. 6. Ball-and-stick models of the 6-ML-high Bi(110) island with the single-layer terrace. The top and side views of the structure are presented in the top and bottom panels, respectively. In the top view, the unit cell of surface Bi atom alignment is indicated by dashed red rectangles on both the 6-ML-high island and the single-layer terrace. The regions with the bulklike and BP-like structures are highlighted by yellow and blue backgrounds, respectively. (a) A model in which both the 6-ML-high island and the terrace have bulklike structures. (b) A model in which the 6-ML-high island has a BP-like structure, while the region under the terrace has a bulklike structure. (c) The novel structure of the Bi(110) island proposed in the study of even-layer-height Bi(110) islands on a graphite substrate [21]. The bulklike layers are sandwiched by the BP-like paired layers at the top and bottom of the islands. The BP-like layers are connected to the bulklike layers by the hypervalent bonds at every second Bi atom in the second layer from the top and bottom. This panel was adapted with permission from P. J. Kowalczyk, O. Mahapatra, S. A. Brown, G. Bian, X. Wang, and T.-C. Chiang, Nano Lett. **13**, 43 (2013). Copyright 2012 American Chemical Society. (d) A model in which the 6-ML-high island has the BP-like structure, while the terrace region has the sandwich structure.

center rectangular unit cell as on the Bi(110) surface. However, the unit cell of the single-layer allotrope (0.39×0.39 nm^2) was compressed and much smaller than that of the bulk and BP-like Bi(110) surface (0.45×0.47 nm^2). In the meantime, the single-layer terrace had the same unit cell size as that of the Bi(110) surface on the even-layer-height Bi(110) islands in this study [Fig. 5(c)]. Thus, the single-layer allotrope is unlikely to be responsible for the single-layer structure observed in this study.

As a possible alternative structure, we consider the novel structure that was proposed in recent density functional theory (DFT) studies of Bi(110) islands [21,22]. Based on DFT calculations, Kowalczyk and coworkers reported that the top two layers possessed a BP-like paired-layer structure in the structural optimization of 3-ML-thick Bi(110) films [22]. The BP-like paired layer was bonded to the bottom layer by hypervalent bonds. Several structural models were proposed based on the various ways of inserting the hypervalent bonds at the boundary between the top BP-like paired layer and the lower layer for the 3-ML-thick Bi(110) film. For thicker Bi(110) films, a more recent DFT study reported a structure in which the bulklike layers were sandwiched by the BP-like paired layers at the top and bottom, as illustrated in Fig. 6(c) [21]. In this structure, the bulklike inner layers are connected to the BP-like layer by the hypervalent bonds at every second Bi atom at the boundary between the BP- and bulklike layers. This structure was proposed for a system in which only the even-layer-height Bi(110) islands nucleated. However, we speculate that the 7-ML-high terrace region also had the sandwich structure in the BP-like 6-ML-high Bi(110) island, as illustrated in Fig. 6(d). In this structure, the zigzag chain in the top BP-like paired layer of the 6-ML-high island is pushed up by a single layer height on the terrace region. The top BP-like layer successfully removes the energetically unfavorable dangling bonds at the island surface. Furthermore, the unit cell on the 7-ML-high sandwich-structured terrace is aligned with that on the 6-ML-high Bi(110) islands with the BP-like structure [Fig. 6(d)], as observed in Fig. 5(c). The hypervalent bonds might not appear at every second Bi atom at the boundary between the BP- and bulklike layers under the 7-ML-high terrace region owing to the various models of insertion reported for the 3-ML Bi(110) film [22]. However, in spite of the various ways of inserting the hypervalent bonds, the unit cell is still aligned between the 6- and 7-ML-high areas in so far as the bulklike inner layers are sandwiched by the BP-like paired layers at the top and bottom of the island. From this perspective, we consider that the odd-layer-height Bi(110) islands possessed the sandwich structure on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate.

In addition to the odd-layer-height islands, the even-layer-height Bi(110) islands may also have the sandwich structure in our system. In fact, a sandwich structure was proposed for even-layer-height Bi(110) islands on a graphite substrate [21]. However, the Bi(110) islands could *not* show the preference for even layer heights in Fig. 3 and the oscillatory behavior of the periodicity in the corrugation in Fig. 4(b) in the case where both the even- and odd-layer-height islands have the same structure. Thus, we consider that the even-layer-height islands had not the sandwich but the BP-like structure in the present system. Although the energetically unfavorable surface dangling bonds are removed, the frustrated hypervalent bonds are still contained in the sandwich structure. The preference for the even-layer-height islands was ascribed to the hypervalent-bond-free inner layers in the BP-like structure.

The odd-layer-height sandwich-structured Bi(110) island could be easily transformed to the even-layer-height BP-like structured island in the presence of a single layer if the Bi atoms are able to flexibly change their bonding between the bulk- and BP-like schemes. The flexible change of the bonding scheme would also enable the transformation of the even-layer-height

BP-like island to the odd-layer-height sandwich-structured island upon the addition of a single layer. Specifically, theoretical calculations have demonstrated flexible switching between BP-like and bulklike bonding with the change of the even-odd parity of the thickness in ultrathin Bi(110) films [13]. Therefore, we speculate that the Bi(110) islands grow by changing the structure between the BP-like and sandwich ones in an alternating manner depending on the even-odd parity of the thickness on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate owing to the flexibility of the bonding scheme. The Bi(110) island takes the energetically preferable BP-like structure if it has an even layer height to allow the stacking of the paired layers. In contrast, it takes the sandwich structure for odd layer heights to eliminate the surface dangling bonds. However, the odd-layer-height island introduces the energetically unfavorable hypervalent bonds to construct the sandwich structure. Thus, the island prefers the even layer heights. This bifurcation of odd-layer-height islands and even-layer-height islands is also explained consistently by the facile transformation of the energetically unfavorable sandwich-structured islands to the energetically favorable BP-structured islands upon the nucleation of the single layer.

The difference in the structure might be reflected in the interlayer distance in the Bi(110) islands. However, no significant alternating change in the interlayer distance was observed between the odd- and even-layer-high Bi(110) islands. In this study, the average interlayer distance was 0.317, 0.316, 0.321, 0.325, and 0.332 nm for the 4-, 5-, 6-, 7-, and 8-ML-high Bi(110) islands, respectively, with an error of ±0.016 nm. These values are consistent with the results of previous experimental studies. The interlayer distance was reported to be 0.325 ± 0.005 and 0.34 ± 0.03 for BP-like Bi(110) islands on Si(111) 7×7 [2] and bulklike Bi(110) islands on Ge(111)$c(2 \times 8)$ substrates [9], respectively. Furthermore, the interlayer distance was reported to be 0.3194, 0.3100, 0.3100, 0.3059, and 0.3045 nm at the top of the 4-ML BP-like, 5-ML bulklike, 6-ML BP-like, 7-ML bulklike, and 8-ML BP-like Bi(110) films, respectively, based on DFT calculations [13]. Although these interlayer distances are slightly smaller than the experimental values, no significant difference was observed between the bulklike odd-layer-height and BP-like even-layer-height Bi(110) films. Therefore, we consider that it is unfortunately not possible to distinguish between the BP-like and sandwich structure with the bulklike inner layers on the basis of the interlayer distance.

D. Electronic states of the Bi(110) islands

The BP-like, bulklike, and sandwich structures all have the same atomic arrangement at their surfaces, as illustrated in Fig. 6. However, the presence of the hypervalent bonds just below the BP layer at the surface might produce characteristic features of the sandwich structure in the STM image, although the influence of the subsurface hypervalent bonds on the STM image has not yet been investigated theoretically. The buckling at the top surface layer was slightly greater on the even-layer-height islands than on the odd-layer-height islands [6]. However, no further differences between the even- and odd-layer-height islands could be discerned in the atomically resolved STM images. Thus, it remains unclear whether the sandwich structure can be distinguished from the BP-like structure based on atomically resolved STM images. However, the difference in the structure must be reflected in the electronic states at the surface. Theoretical studies predicted that the Dirac cone appears at the $\bar{M}$ point owing to the periodic arrangement of the dangling bonds on the bulklike Bi(110) surface. At the same time, a band gap opens at the $\bar{M}$ point on the BP-like Bi(110) surface without surface dangling bonds [13,14]. In these respects, the structure of the island is expected to be identifiable by observing the surface band dispersion. However, the Bi(110) islands were nucleated randomly along the six rotational orientations (Fig. 2). Furthermore, islands of various heights coexisted in the present system. These make it difficult to observe the surface dispersion using angle-resolved photoelectron spectroscopy. As an alternative, in this study we used STS to investigate the local electron density of states (DOS) of the Bi(110) islands.

Figure 7 shows the averaged spectrum of 100 STS spectra of the Bi(110) islands. In the left column, the averaged STS spectra are presented for islands with heights from 4 to 8 ML. For comparison, the middle column shows the theoretically calculated electron DOSs of freestanding Bi(110) ultrathin films [13]. The DOSs of the 4-, 6-, and 8-ML-high islands were calculated by assuming a BP-like structure, while those of the 5- and 7-ML-high islands were calculated by assuming a bulklike structure. Thus, the theoretical DOS decreased at around the Fermi level for the even-layer-height BP-like films with the band gap. In contrast, it increased for the odd-layer-height bulklike films with the Dirac cone. As a result, the DOS around the Fermi level oscillates alternately in accordance with the change of the even-odd layer height in the theoretical calculation. The alternating change of the DOS around the Fermi level is remarkable, particularly for the increase in the height from 4 to 6 ML. However, such a change in the DOS was not observed around the Fermi level in the STS spectra of the Bi(110) islands on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate. The STS intensity was consistently small at around the Fermi level in this experiment. The result is consistent with a BP-like structure for the even-layer-height Bi(110) islands. However, the odd-layer-height islands are again considered not to have the bulklike structure with respect to the STS intensity around the Fermi level.

The intrinsic electronic states of the Bi(110) islands might be modified by the interface strain at the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate in the present system. However, the Bi(110) islands grew commensurately so as to align the diagonal of their unit cells to the diagonal of the substrate $\sqrt{3} \times \sqrt{3}$ unit cell with a misfit as small as 0.2% [6]. Meanwhile, a recent theoretical study of the BP-like Bi(110) paired layer demonstrated that the band gap changes with the in-plane strain at a rate of 1–2 meV/% [24]. Thus, we consider it reasonable to disregard the strain-induced effect in the above comparison between the STS spectra and the theoretical DOS of the freestanding Bi(110) films.

The peaks in the STS spectra also support the BP-like structure for the even-layer-height Bi(110) islands. The peak positions are indicated by arrows in both the STS spectra and theoretical DOSs of Bi(110) films in Fig. 7. The peaks in the STS spectra were found to coincide with the theoretically calculated DOSs, which were shifted upward by 0.13 eV for

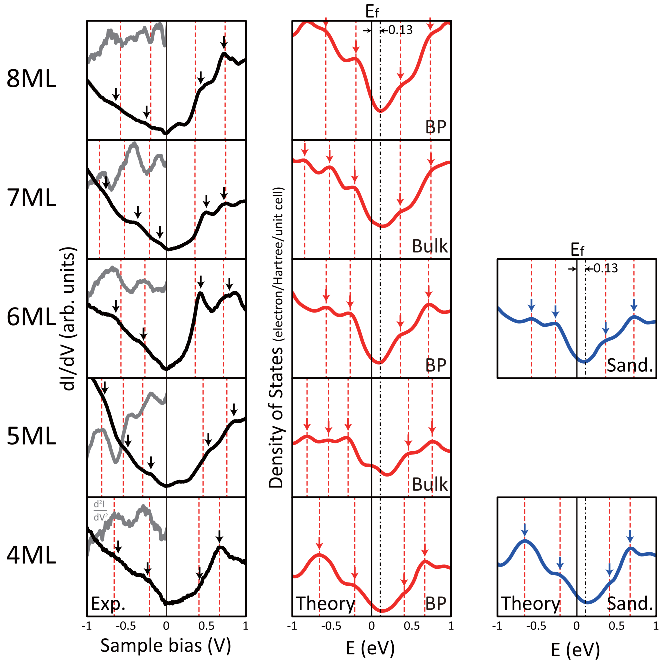

FIG. 7. Left column: STS spectra of Bi(110) islands on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate. The island thickness is indicated on the left side. Each spectrum is the average of 100 individual STS spectra. The set point was $V_s = -1.0\,\mathrm{V}$, $I_t = 0.5\,\mathrm{nA}$. Second derivatives of the STS spectra are indicated in gray. Middle column: Theoretically calculated DOSs of freestanding Bi(110) films in Ref. [13]. The 4-, 6-, and 8-ML-high Bi(110) films were assumed to have the BP-like structure, whereas the bulklike structure was assumed for the 5- and 7-ML-high Bi(110) films. Right column: Theoretically calculated DOSs of 4- and 6-ML-high Bi(110) films with the sandwich structure in Ref. [19]. The peaks are indicated by arrows in the STS spectra and theoretical DOSs. At each island thickness, the dashed red vertical lines indicate the peak position of the theoretical DOS in the middle column. The DOSs in the middle and right columns are reproduced with permission. (Middle column: adapted with permission from G. Bian, X. Wang, T. Miller, T. -C. Chiang, P. J. Kowalczyk, O. Mahapatra, and S. A. Brown, Phys. Rev. B **90**, 195409 (2014). Copyright 2014 American Physical Society. Right column: adapted with permission from P. J. Kowalczyk, O. Mahapatra, S. A. Brown, G. Bian, X. Wang, and T.-C. Chiang, Nano Lett. **13**, 43 (2013). Copyright 2012 American Chemical Society.)

the even-layer-height Bi(110) films. This shift was ascribed to the electron charge transfer from the Bi island to the highly B doped p-type Si substrate in the present system. The peak positions of the shifted DOSs are indicated by the vertical dashed lines in the STS spectra. Satisfactory agreement was observed, as shown by the arrows and the vertical dashed lines in the left column.

In contrast, for the odd-layer-height Bi(110) islands, the peaks in the STS spectra did not agree with those in the DOSs. This disagreement once again ruled out a bulklike structure for the odd-layer-height islands. However, the DOS has not been theoretically calculated for the odd-layer-height Bi(110) films with the sandwich structure. Thus, we cannot confirm that the odd-layer-height Bi(110) islands have the sandwich structure based on the peak positions in the STS spectrum. However, the occurrence of the sandwich structure for the odd-layer-height islands is supported by the consistently small STS intensity at the Fermi level. Bian and coworkers revealed that the Dirac-cone-like dispersion appears at $\bar{M}$ by the periodic arrangement of the Bi p_z dangling bonds with mirror symmetry along the long side of the rectangular unit cell at the bulklike Bi(110) surface in their calculations for a one-atomic-layer Bi(110) film [13]. It is the Dirac-cone-like dispersion that causes the theoretically predicted increase in the DOS at the Fermi level of the Bi(110) films with the bulklike structure. However, the top surface is terminated by the BP-like paired layer without surface dangling bonds in the sandwich structure. Thus, the sandwich-structured Bi(110) island is expected to exhibit a small STS intensity around the Fermi level as well as the BP-structured Bi(110) island. The theoretically calculated DOSs of the sandwich-structured Bi(110) films with heights of 4 and 6 ML [21] are shown in the right column of Fig. 7. The DOS of the sandwich structure is almost identical to that of the BP-like structure, probably because the top surface is terminated by the BP-like paired layer in both cases. The available theoretical DOS of the sandwich structure is limited to the even-layer-height films at the moment. However, the top of the odd-layer-height sandwich-structured Bi(110) island is also terminated by the BP-like paired layer. In this respect, the lack of increase in the STS signal around the Fermi level is consistent with the sandwich structure for the odd-layer-height islands.

E. Individuality of the wetting layer

The islands were nucleated on the 1-ML-thick wetting layer in the present system. The crystallization of the wetting layer under the islands is feasible, as discussed in Sec. III A. If this wetting layer were included, the island height would increase by 1 ML, and the even-odd-layer-height relation would be reversed. However, the Bi(110) islands preferred the even layer height on the wetting layer. This strongly suggests that the wetting layer was not involved in forming the first BP-like structured paired layer at the bottom of the island. The specificity of the wetting layer was investigated theoretically for the Bi(110) films by Bian *et al.* [13]. They simulated the bonding of the films to the substrate by the hydrogen termination of the bottom layer in freestanding Bi(110) films. The calculation revealed that the paired layers of the BP-like structure form over the hydrogen-terminated bottom layer. The hydrogen-terminated bottom layer was not involved in forming the upper paired layers of the BP-like structure. Therefore, the wetting layer was not involved in forming the BP-like paired layer at the bottom of the Bi(110) island owing to the specific bonding to the substrate in our system.

IV. SUMMARY

In summary, we investigated the nucleation and growth of ultrathin Bi(110) islands on the Si(111)$\sqrt{3} \times \sqrt{3}$-B substrate by STM. The islands formed both even and odd layer heights in the growth process. However, the islands preferred even layer heights over odd layer heights with an area ratio of 3:1. The nucleation of single- and paired-layer terraces was observed on the even-layer-height islands but not on the odd-layer-height islands. The absence of displacement of the unit cell on the single-layer terrace on the 6-ML-thick islands ruled out the possibility that the island adopted a bulklike structure during the entire nucleation and growth. The dominance and stability against the overlayer nucleation of the even-layer-height islands were attributed to the BP-like structure. Importantly, the STS spectra coincided with the theoretically calculated DOS of the BP-like structure for the even-layer-height Bi(110) islands. In contrast, the STS spectra did not agree with the theoretically calculated DOS of the bulklike structure for the odd-layer-height islands in terms of either the intensity around the Fermi level or the peak positions. However, the BP-like/bulklike/BP-like sandwich structure consistently explained the lack of increase in the STS signal around the Fermi level and the absence of a shift of the unit cell on the odd-layer-height Bi(110) islands. The 1-ML-thick wetting layer was not involved in the BP-like island structure owing to the specific bonding to the substrate.

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[1] Y. Lu, W. Xu, M. Zeng, G. Yao, L. Shen, M. Yang, Z. Luo, F. Pan, K. Wu, T. Das, P. He, J. Jiang, J. Martin, Y. P. Feng, H. Lin, and X. Wang, Nano Lett. **15**, 80 (2015).

[2] T. Nagao, J. T. Sadowski, M. Saito, S. Yaginuma, Y. Fujikawa, T. Kogure, T. Ohno, Y. Hasegawa, S. Hasegawa, and T. Sakurai, Phys. Rev. Lett. **93**, 105501 (2004).

[3] J. T. Sadowski, T. Nagao, S. Yaginuma, Y. Fujikawa, T. Sakurai, A. Oreshkin, M. Saito, and T. Ohno, J. Appl. Phys. **99**, 014904 (2006).

[4] G. Bian, T. Miller, and T.-C. Chiang, Phys. Rev. B **80**, 245407 (2009).

[5] S. Yaginuma, K. Nagaoka, T. Nagao, G. Bihlmayer, Yu. M. Koroteev, E. V. Chulkov, and T. Nakayama, J. Phys. Soc. Jpn. **77**, 014701 (2008).

[6] I. Kokubo, Y. Yoshiike, K. Nakatsuji, and H. Hirayama, Phys. Rev. B **91**, 075429 (2015).

[7] S. Yaginuma, T. Nagao, J. T. Sadowski, M. Saito, K. Nagaoka, Y. Fujikawa, T. Sakurai, and T. Nakayama, Surf. Sci. **601**, 3593 (2007).

[8] D. Lükermann, S. Banyoudeh, C. Brand, S. Sologub, H. Pfnür, and C. Tegenkamp, Surf. Sci. **621**, 82 (2014).

[9] S. Hatta, Y. Ohtsubo, A. Miyamoto, H. Okuyama, and T. Aruga, Appl. Surf. Sci. **256**, 1252 (2009).

[10] C. Koitzsch, M. Bovet, F. Clerc, D. Naumovic, I. Schlapbach, and P. Aebi, Surf. Sci. **527**, 51 (2003).

[11] P. J. Kowalczyk, O. Mahapatra, D. N. McCarthy, W. Kozlowski, Z. Klusek, and S. A. Brown, Surf. Sci. **605**, 659 (2011).

[12] J.-T. Sun, H. Huang, S. L. Wong, H.-J. Gao, Y. P. Feng, and A. T. S. Wee, Phys. Rev. Lett. **109**, 246804 (2012).

[13] G. Bian, X. Wang, T. Miller, T.-C. Chiang, P. J. Kowalczyk, O. Mahapatra, and S. A. Brown, Phys. Rev. B **90**, 195409 (2014).

[14] Y. M. Koroteev, G. Bihlmayer, E. V. Chulkov, and S. Blügel, Phys. Rev. B **77**, 045428 (2008).

[15] H. Fukumoto, Y. Aoki, and H. Hirayama, Phys. Rev. B **86**, 165311 (2012).

[16] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).

[17] Y. Chen, M. W. Gramlich, S. T. Hayden, and P. F. Miceli, Phys. Rev. Lett. **114**, 035501 (2015).

[18] Y. Chen, M. W. Gramlich, S. T. Hayden, and P. F. Miceli, Phys. Rev. B **94**, 045437 (2016).

[19] T. L. Ho, C. Z. Wang, M. Hupalo, M. C. Tringides, W. C. Lu, and K. M. Ho, Surf. Sci. **600**, 1093 (2006).

[20] C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14419 (1992).

[21] P. J. Kowalczyk, O. Mahapatra, S. A. Brown, G. Bian, X. Wang, and T.-C. Chiang, Nano Lett. **13**, 43 (2013).

[22] P. J. Kowalczyk, D. Belic, O. Mahapatra, S. A. Brown, E. S. Kadantsev, T. K. Woo, B. Ingham, and W. Kozlowski, Appl. Phys. Lett. **100**, 151904 (2012).

[23] P. J. Kowalczyk, O. Mahapatra, M. Le Ster, S. A. Brown, G. Bian, X. Wang, and T.-C. Chiang, Phys. Rev. B **96**, 205434 (2017).

[24] S. S. Li, W. X. Ji, S. J. Hu, L. Cai, C. W. Zhang, and S. S. Yan, Appl. Mater. Interfaces **9**, 21515 (2017).