Electronic structure and surface-mediated metastability of Bi films on Si(111)-7×7 studied by angle-resolved photoemission spectroscopy

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We have observed using angle-resolved photoemission a structural phase transformation of Bi films deposited on Si(111)-7×7. Films with thicknesses 20 to ~100 Å, upon annealing, first order into a metastable pseudocubic (PC) phase and then transform into a stable rhombohedral (RH) phase with very different topologies for the quantum-well subband structures. The PC phase shows a surface band with a maximum near the Fermi level at $\bar{\Gamma}$, whereas the RH phase shows a Dirac-like subband around $\bar{M}$ along $\bar{K}-\bar{M}-\bar{K}$. The formation of the metastable phase over a wide thickness range can be attributed to a surface nucleation mechanism.

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I. INTRODUCTION

Semimetallic Bi has attracted intense interest because of its unique combination of physical properties including a strong spin-orbit coupling, a large Fermi wavelength, and a small Fermi surface with Dirac-like band features that are tunable by doping or alloying.[1–4] These attributes make Bi a promising candidate for electronic and spintronic applications.[5] In the present work, we report the observation of a metastable pseudocubic (PC) phase of Bi films made by annealing initially disordered films of thicknesses 20 to ~100 Å deposited on Si(111)-7×7 at low temperatures. The metastability of the PC phase is demonstrated by the transformation, upon annealing to higher temperatures, to the stable rhombohedral (RH) bulk phase. The two phases are easily distinguished by angle-resolved photoemission as they exhibit different surface states and quantum-well subbands.[6] While the electronic structure of the RH phase has been well characterized in prior studies,[7–9] the present work provides the first detailed experimental mapping of the surface states and the quantum-well subbands in the metastable PC phase. It is interesting to note that the two phases have nearly the same atomic volume, but the measured band topologies are very different. Specifically, the curvatures of the subbands at the zone center $\bar{\Gamma}$ have opposite signs. The RH phase shows a Dirac-like subband around $\bar{M}$ along $\bar{K}-\bar{M}-\bar{K}$,[10,11] which is absent in the PC phase. A bundle of surface states in the RH phase below the Fermi level is replaced by a concave surface band in the PC phase that moves slightly upward and pokes through the Fermi level with increasing film thicknesses. These observations are in generally good accord with first-principles slab calculations.

The metastable behavior is observed over a film thickness range from 20 to ~100 Å. Below 20 Å, the film's structure after annealing is always the PC phase; above ~100 Å, the only stable phase is RH. For comparison, previous scanning tunneling microscopy (STM) work on Bi films reported a surface structure identified as that of the PC phase for film thicknesses equal to or less than four bilayers (BL) (13 Å; see below for an explanation of the bilayer); thicker films showed a surface structure consistent with the RH phase.[12,13] The critical thickness of 4 BL was attributed to a crossover of the relative importance of the surface and bulk energies of the films, with the PC phase having a lower surface energy. Evidently, the previous STM study did not look specifically for metastable structures, and our study shows that the critical thickness is 6 BL instead. At the upper thickness limit of metastability (~100 Å), the surface bilayer constitutes just ~4% of the system; this has strong implications regarding the energetics of the metastable-to-stable phase transformation.

II. EXPERIMENTAL DETAILS AND COMPUTATIONAL METHODS

In our experiment, an *n*-type Si(111) wafer (Sb-doped with a resistivity ~0.01 Ω·cm) was used as the substrate. It was cleaned by direct current heating to yield a (7×7) reconstructed surface. Bi was deposited onto the substrate maintained at 60 K. The amount of deposition was measured by a quartz thickness monitor. The film after deposition was disordered based on *in situ* electron diffraction. Annealing was performed by passing a current through the sample. Photoemission measurements of the band structure were performed at the Synchrotron Radiation Center using 22 eV photons and a hemispherical analyzer (Scienta SES-100) equipped with a two-dimensional detector.

For comparison with the experimental results, we performed first-principles slab calculations of the electronic structure of the films using Hartwigsen-Goedecker-Hutter pseudopotentials and a plane-wave basis set;[14] the main program employed was developed by the ABINIT group.[15] Appropriate surface relaxation parameters were included in the structural model.[16] Spin-orbit coupling, which is crucial for the description of the electronic structures of heavy elements such as Bi, was included in the calculation.

III. RESULTS AND DISCUSSION

Figure 1 shows model drawings of the PC and RH structures;[7,16] each can be described in terms of a stack of BLs, where each BL contains two closely spaced atomic lay-

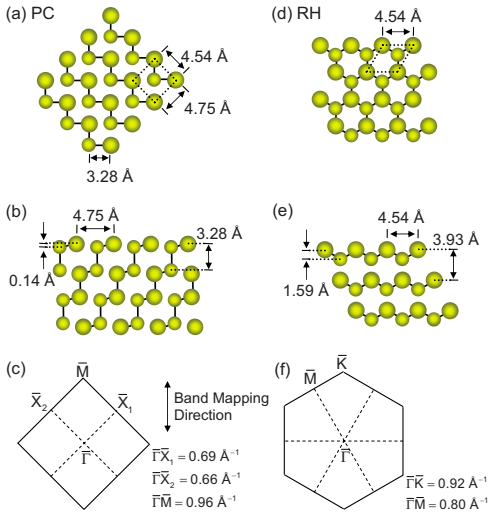

FIG. 1. (Color online). (a) Top view of (110), (b) side view along $[1\bar{1}0]$, and (c) surface Brillouin zone of the PC structure. (d) Top view of (111), (e) side view along $[11\bar{2}]$, and (f) surface Brillouin zone of the RH structure. Larger balls indicate atoms closer to the viewer. The direction of photoemission band mapping is indicated.

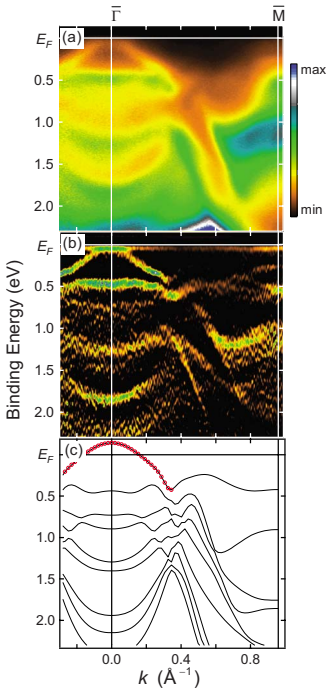

FIG. 2. (Color online). (a) Photoemission results from a 6 BL Bi film in the PC phase. (b) Second derivative along the energy axis of the photoemission data to enhance the contrast. (c) Calculated band structure. The top band, marked by small circles, has a surface character.

ers. The RH films are oriented along [111]. Currently there are two proposed structural models for the PC phase: one is a black-phosphorus-like structure and the other is a slightly expanded (by ~1%) bulk-like structure oriented along [110]. The differences between the two models are fairly minor,[17] but the latter matches our data slightly better and is shown in Fig. 1. Within this model, the PC and RH films have similar bulk structures but different crystallographic orientations. The atomic density of 1 BL is 1.12×10^{15} atoms/cm^2 for the RH phase and 9.27×10^{14} atoms/cm^2 for the PC phase; thus, 1 BL of RH is equivalent to 1.21 BL of PC. The nominal thickness of each BL is 3.93 Å for the RH phase and 3.28 Å for the PC phase. The PC to RH transformation thus involves a rather unusual rearrangement of the incommensurate layer structures. In the following, we will refer to the film thickness in terms of either the PC BL or the RH BL, where appropriate. The surface Brillouin zones for the two phases are shown in Fig. 1; the direction mapped by the photoemission measurements corresponds to the $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{K}$ directions of the PC and RH phases, respectively.

Figure 2(a) shows photoemission results for a 6 BL PC film obtained by annealing to 350 K; this thickness is the upper limit of stability for PC. Figure 2(b) shows the same data differentiated twice along the energy axis. This differentiation effectively removes a background and enhances the contrast for a better visualization of the band dispersions. Figure 2(c) is the results of our first-principles slab calculation for comparison. Overall, there is a good agreement between the present calculation, a previous calculation,[16] and the experiment. Experimentally, the top subband (marked by small circles) has a concave shape near $\bar{\Gamma}$ and nearly grazes the Fermi level. A comparison of the calculated slab band structure to a calculated projected bulk band structure reveals that this band has a surface character near $\bar{\Gamma}$ (see below for further evidence). While this band is fully occupied based on the experiment, the calculation puts it slightly higher, resulting in a hole pocket at $\bar{\Gamma}$. The experiment and calculation agree that the next few subbands below are nearly flat near $\bar{\Gamma}$ and the ones further below become convex.

Figure 3(a) presents the photoemission results from a film of thickness equivalent to 20 BL in the PC phase or 17 BL in the RH phase. After deposition, the film was annealed to 280 K and cooled back to 60 K; its structure is PC. The second derivative of the data is present in Fig. 3(b). The results are similar to those seen in Fig. 2, but with more densely packed quantum-well subbands as expected. The top subband near $\bar{\Gamma}$, indicated by circles, is distinctly separated from the others because of its surface character. Compared to the 6 BL case, it has moved slightly upward to create a small hole pocket at $\bar{\Gamma}$. These features are generally consistent with the theoretical results shown in Fig. 3(c). The calculation shows pairs of subbands near $\bar{\Gamma}$, which arise from a pair of closely spaced bulk bands of Bi along the $\Gamma-X$ direction.[11] The energy difference in each pair is too small to be resolved experimentally; thus, each pair appears in the experiment as a single broadened subband.

Figure 4 presents theoretical evidence for the surface and bulk characters of the various states. The upper panel shows a detailed view of the band structure near the Fermi level for a 20 BL Bi film in the PC phase; several states A–E are marked. The corresponding plane-averaged charge densities for these states are shown in the lower panel. Evidently, states A and B are derived from bulk states, while states C–E

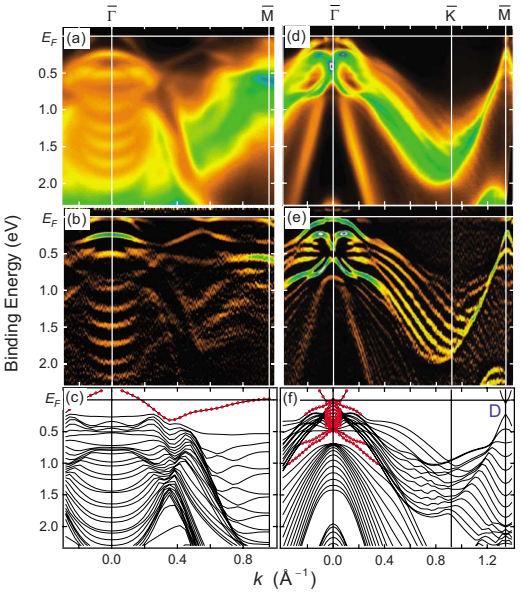

FIG. 3. (Color online). (a) Photoemission data and (b) second derivative taken from a Bi film of thickness equivalent to 20 BL in the PC phase or 17 BL in the RH phase after annealing to 280 K. The structure of the film is PC. (c) Calculated band structure for the PC phase. (d) Photoemission data and (e) second derivative taken from the same film after annealing to 350 K. The structure of the film is RH. (f) Calculated band structure for the RH phase; the label "D" marks a Dirac-like feature. Surface states are indicated by small circles in (c) and (f).

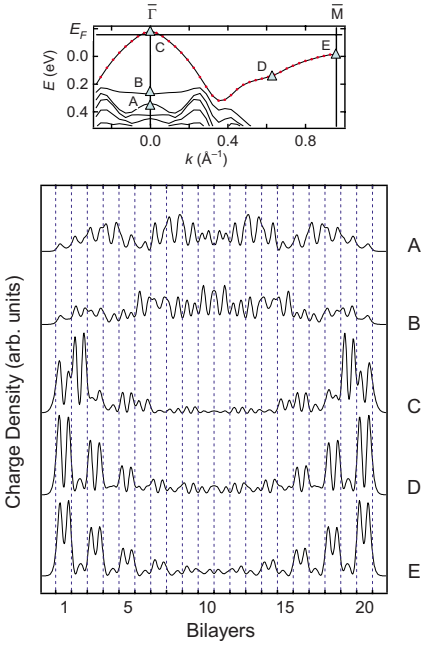

FIG. 4. (Color online). Upper panel: calculated electronic structure of a 20 BL film in the PC phase. Five states A–E are marked. Lower panel: the plane-averaged electronic charge densities within the film for the five states. The vertical dashed lines separate the bilayers.

are surface states as they decay away from the surfaces. The decay lengths of the surface states are quite long; at small film thicknesses, the charge distributions localized near the two surfaces join, and a charge-density plot alone is insufficient to make a positive identification of the surface character.

The photoemission spectra from the same film change dramatically after annealing to 350 K, as seen in Fig. 3(d) and its second derivative in Fig. 3(e). The set of convex quantum-well subbands near $\bar{\Gamma}$ at binding energies 1–2 eV for the PC phase have disappeared. Instead, one observes a bundle of closely packed concave bands with complex structures near $\bar{\Gamma}$. For comparison, Fig. 3(f) presents the results of our slab calculations for the RH structure with the surface states indicated by small circles. The similarities between the experiment and theory are apparent, thus, confirming the RH structure of the film. Our results also agree with a previous photoemission mapping of the bands for the RH phase.[7,8] The calculated results in Fig. 3(f) show a bunch of surface states at low binding energies near $\bar{\Gamma}$. This is seen in photoemission as an intense peak at ~0.4 eV.

Of special interest are the bands near $\bar{M}$, where there is an excellent agreement between the calculation and experiment. Near the Fermi level, a small gap, marked by D, separates a Λ shaped lower band and a V-shaped upper band. These dispersion relations are nearly Dirac-like along $\bar{K}-\bar{M}-\bar{K}$. In the bulk limit, the region under the Λ shaped band is completely filled with bulk states. Quantum size effects lead to discretization of the bulk band continuum and bring about the Dirac-like dispersion. The present work suggests that quantum size effects could be an additional mechanism for modifying the band structure and realizing Dirac physics in low-dimensional systems.

Experimentation with various film thicknesses has established the PC-RH metastability regime to range from 20 to ~100 Å (6 BL PC phase to ~27 BL RH phase). The transformation from PC to RH is illustrated by the results presented in Fig. 5. The top row displays photoemission data from a 14 BL (referred to the RH phase) Bi film recorded at

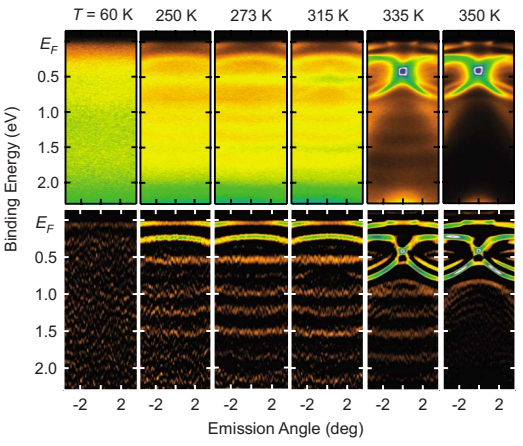

FIG. 5. (Color online). Top row: Photoemission results from a Bi film of thickness 14 BL (referred to the RH structure) after annealing to various temperatures as indicated. The structure of the film changes from a disordered phase to the PC phase first, then to a mixed phase, and finally to the RH phase. Bottom row: Second derivative of the same data.

various sample temperatures while the sample temperature was raised slowly. The corresponding second derivatives are shown in the bottom row. The spectra taken before annealing are featureless because of structural disorder. Features associated with the PC phase emerge around 250 K and become fully developed at ~300 K. Further annealing to 315–335 K results in a mixture of the PC and RH phases, as one can detect the characteristic subband dispersions of both phases in the data. Annealing to 350 K fully converts the film to the RH phase. Annealing to even higher temperatures leads to broadening and fading of the subbands, which can be attributed to thermal roughening of the film.

An inspection of the data in Fig. 5 reveals that the quantum-well subbands for the PC phase remain at the same energy positions throughout the gradual transition to the RH phase. If the phase transformation begins at the surface or interface of the film and propagates thickness wise, one would expect the quantum-well subband structure of the PC phase to evolve in accordance with a gradual reduction in film thickness. This is clearly not the case based on the experiment. We conclude that the transformation mainly involves the formation of lateral domains that expand laterally as the annealing progresses.

Previous studies have proposed that the PC structure is stable at lower thicknesses because it has a lower surface energy (but a higher bulk energy).[12,13] As the film thickness increases, the surface contribution diminishes relative to the bulk contribution and the total energy of PC becomes higher than that of RH at thicknesses greater than 6 BL (or 4 BL based on the previous STM study). But why does the PC phase persist as a metastable phase to a rather large film thickness of ~100 Å? A physical picture is as follows. As an initially disordered film is annealed, it is likely that the atoms at the surface become mobile first because of the reduced coordination. The surface atoms tend to adopt the PC structure locally for its lower energy and the ordering then propagates throughout the film resulting in a metastable PC film. Thus, the metastable phase formation is likely a kinetic effect associated with surface nucleation. Annealing to higher temperatures causes the system to make a transformation to the stable phase. The annealing temperature needed for this transformation, ~350 K, corresponds to just 30 meV, a very small thermal energy. This suggests that the barrier for the phase transformation is very low. Furthermore, the metastable phase persists to a large thickness (~100 Å) at which the surface bilayer constitutes just ~4% of the film. This suggests that the difference in bulk energies between the two phases is very small; otherwise thermal fluctuations could readily bring the system over the barrier and down a steep energy slope, thus severely restricting the range of metastability. The near degeneracy of the bulk energy is consistent with the observation that the two phases have nearly the same bulk structure, the main difference being a slight expansion by ~1% of the PC phase. It is interesting to note a somewhat analogous behavior of another group V element, P, which exhibits a PC-RH transition upon compression under pressure.[18,19]

IV. CONCLUDING REMARKS

In summary, the present study based on photoemission demonstrates the existence of a metastable PC phase and a stable RH phase of Bi films over a wide range of film thickness from 20 to ~100 Å. Below 20 Å, PC is the only ordered phase observed; above ~100 Å, RH is the only one. The quantum-well subband structures for the two phases have very different topologies, which make a positive identification of the phases straightforward. This is a much more robust identification of the internal film structure than STM or electron diffraction observation of the (near) surface atomic geometry. The complex electronic structures of the two phases as determined by photoemission are confirmed by first-principles slab calculations. Among the many interesting electronic features, the PC phase has a surface band at $\bar{\Gamma}$ that grazes the Fermi level, while the RH phase has a Dirac-like subband at $\bar{M}$ along $\bar{K}-\bar{M}-\bar{K}$. The PC-RH metastability range of 20 to ~100 Å is unusually wide, but it can be understood in terms of a near degeneracy of the bulk energies of the two phases and a surface nucleation process that facilitates the formation of the metastable phase. Subbands in thin films can be tuned by changing the film thickness; together with metastability, the results suggest opportunities for fine tuning the electronic structure of Bi films, a system of interest for spintronic applications.

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