Supporting Information for

“Evidence of topological edge states in buckled antimonene monolayers”

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Figure S1. Atomic structure of first buckled antimonene monolayer (BAM) on Cu(111) substrate. (a) Structural model, STM simulation, and atomically resolved topography of BAM. The unit cells are marked by blue diamonds. Both antimony atoms of the BAM can be recognized in the STM image (right) and STM simulation (center). (b) Side view of the atomic model in panel a. (c) Cross-sectional electron localization function (ELF) along the green arrow in panel a, demonstrating high localization of the electrons in Sb-Sb pairs and weak Sb-Cu interaction. These results provide a strong support for the structural characterization described in Fig. 1 in the main text.

The adsorption structures of the BAM on the Cu(111) substrate are calculated by the method that is conventionally adopted in the research field of surface science. In detail, four adsorption sites, namely hcp, fcc, bridge, and top sites, with respect to the hexagonal center of the BAM are considered. The calculations show that the favorable adsorption site of BAM on Cu(111) surface is hcp. Thus, the minimal separation between BAM and Cu(111) is 2.36 Å, which is slight smaller than the physisorption separation. We found that the slightly close separation here does not significantly change the emergence and position of the Dirac point as described in Fig. 2e in the main text. We further observed that the thickness of the Cu(111) substrate (three, ten, and twenty layers are used here) does not influence the band structures, Rashba effect, and surface-protected topological edge states (TES).
Figure S2. XPS and LEED results for the Cu(111) substrate. (a) The XPS spectrum of copper substrate. Two intrinsic $2p$ core peaks locate at 932.57 eV and 952.39 eV. (b) LEED pattern of a clean Cu(111) substrate showing six sharp points, showing the same feature as the outer cycle of points in Figure 1f in the main text.

Apart from the XPS spectrum of Sb-4$d$ peaks, the spectrum of Cu-2$p$ peaks applies another evidence for that there is no intermixing between antimony and copper. As show in Figure S2a, the Cu-2$p_{3/2}$ peak located at the energy of 932.57 eV is agree well with the peak measured on copper crystal $^{1,2}$, proving that no chemical property and atomic structure changes in the substrate. We also measured the LEED on the clean Cu(111) substrate before the fabrication of BAM as shown in Figure S2b. The LEED pattern with six diffractive dots give a direct comparation with the one shown in Figure 1f, confirming the Cu(111) - $(\sqrt{3} \times \sqrt{3})$R30º superstructure of antimonene.
\[ \delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i) \]

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Figure S3. \( Z_2 \) invariants of the freestanding antimonene monolayer. The parities of each band of interest are listed in the table. The semicolons are used to distinguish the occupied and empty bands. The observation of the topological properties of the BAM is limited to the second conduction band (CB2), which is denoted by the comma. The parity for each time-reversal-invariant momentum point is obtained either by analyzing the wavefunction coefficients in VASP or by calculating the band symmetry implemented in Quantum ESPRESSO (QE). The VASP and QE programs provided identical results for each parity. These calculations fully support the topological properties described in Figs. 2a-c in the main text.
Figure S4. Band structure, density of states (DOS), and experimental dI/dV values of the freestanding and supported buckled antimonene monolayers. (a) Band structure for freestanding BAM, which is a zoom-out pattern of that shown in Fig. 2a in the main text. (b) The measured dI/dV spectrum at the center of the antimonene nanoisland. (c) Band structure of the copper-supported BAM, which is a zoom-out pattern of that shown in Fig. 2d in the main text. Since the whole BAM on Cu(111) has broken the inversion symmetry and the entangled band structures, it is computationally expensive to calculate its Wannier charge center (WCC) in the Brillouin zone and the well-defined $\mathbb{Z}_2$ invariant. The edge states of the BAM nanoribbon on the Cu(111) surface are studied using iterative Green’s function.\textsuperscript{3-6} (d) The measured dI/dV spectrum on the BAM corresponds to the lower branch of the Rashba bands. The red curve is the calculated DOS around CB2, which matches well with the experimental dI/dV spectrum (black curve), providing a strong support for the discussion in the second part of the results in the main text. The DOS integral is performed on a squared patch of momentum $k$ points marked in green in panel c.
Figure S5. The calculated band structures of two BAM on a ten-layer Cu(111) projected on (a) the top BAM, (b) the first BAM and (c) the underneath copper substrate. The spin-orbit coupling is included. The weight summed over the layer of interest is represented by the color dots. The figures show basically no overlapping region (shaded area) between panels a (top layer) and c (copper substrate), proving that the copper substrate hardly affect the second layer BAM.

We investigate the influence from the copper substrate via the calculation of the model with two BAMs supported by copper substrate. Three panels of separated band structures illustrate the contribution from different layers. The first BAM (Figure S5b) have obvious overlapping with both the top layer BAM (Figure S5a) and the copper substrate (Figure S5c). However, the band structures of the top layer BAM and the copper substrate show little overlapping region, indicating the buffering role of the first layer antimonene.
Figure S6. The spatial expansion of topological edge states. (a) The electronic structures and topological edge states (blue line) of a free-standing antimony nanoribbon of width 66.5 Å. The spin-orbit coupling is included in all the calculations. (b) The real space partial charge density of topological edge states on the Γ point is distributed around the edge. The upper, middle and lower panel are the top view, side view and planar averaged charge density along ribbon width direction respectively. The periodic direction of the antimony nanoribbon is denoted by a blue arrow in top view of panel b. The expanding distance marked by red lines is 10 Å, which is agree well with the experimental results shown in Figure 3d of the main text.
Figure S7. Band structures, edge states, and WCC (Φ) with varying lattice constants.

Summary of the DFT calculations of the band structure for the freestanding BAM with varying lattice constants (4.3 Å, 4.4 Å and 4.7 Å). The WCC is defined by $\Phi_n = \frac{i}{2\pi} \int_{-\pi}^{\pi} dk \langle \varphi_n | \partial_k | \varphi_n \rangle$, where $| \varphi_n \rangle$ is the periodic part of the plain wave function of the electronic states of interest. If the arbitrary horizontal reference line crosses the WCC by an odd number of times, it evidences the topological nontrivial nature of the energy band; otherwise it indicates the opposite.

We tune the tensile strain by increasing the lattice constant from the freestanding condition. When the lattice constant increases to 4.7 Å, a new topological edge state emerges at the Fermi level. This was also reported in a previous work. However, considering the band structure above the fermi surface, there is a robust TES between CB1 and CB2 when tuning the tensile strain.
References


