Supplementary Informations for
Robust topological edge states and superconductivity
in few-layer stanene

I. Methods.
II. Stacking manner between stanene layers.
III. Configurations and formation energies of stanene films on Bi(111).
IV. Band structures of stanene films with different layer thicknesses.
V. Spatially resolved $\Delta$LDOSs.
I. METHODS

1. Sample growth

FIG. S1. Growth of stanene films on Bi (111). a, Topography of Bi(111) substrate. \( \Delta t \) means the duration of annealing process. b, Variation of sample surface during the annealing process at room temperature after the low temperature deposition of Sn atoms. c, Topographies of stanene films by annealing process at 40\(^\circ\)C.

The Bi(111) substrate was obtained by molecular beam epitaxy on a silicon wafer at room temperature in the preparation chamber with base pressure of \( 2 \times 10^{-10} \) torr. An annealing treatment at 135\(^\circ\)C was applied straight after the growth, and it would last for more than 10 hours to make the Bi(111) films flat and large enough. The deposition of Sn was carried out at low temperature to prevent the formation of accumulational clusters. Both Bi and Sn sources are knudson diffusion cells with a high purity of 99.9999\%. Before depositing Sn, the sample [namely, the Bi(111) on silicon wafer] was cooled down to liquid helium temperature of \( \sim 4.2 \) K in STM chamber. Then it would be quickly transferred to the preparation chamber.
to deposite Sn. The deposition of Sn lasts for at most 3 minutes for each time to prevent the sample from warming up too much. The left panel of Fig. S1b shows the as-grown Sn atoms (deposition for 2 mins), where the Sn atoms evenly cover the surface of Bi(111). Then an annealing process at room temperature was applied. With increasing the annealing time, the Sn atoms gradually form stanene islands.

However, the annealing process at room temperature takes too much time. We tried to accelerate this process by raising the annealing temperature to 40°C. As shown in Fig. S1c, the Sn atoms form stanene islands within only 20 mins by annealing at 40°C. It should be noted that the annealing temperature should be lower than 138°C, above which the Sn and Bi would mix together to form Sn-Bi alloy. When the coverage of the stanene islands exceeds ∼ 50 %, the isolated islands would merge together to form large films, as shown in Fig. S1c. Forming a whole layer stanene film needs the deposition of Sn of ∼8 minutes in total.

2. STM measurements

In-situ STM measurements are carried out after sample growth. The STM chamber has a base pressure of 1×10⁻¹⁰ torr. The sample is cooled down to 4.2 K for all the measurements of topological edge states and 400 mk for the measurements of superconductivity. The topographic images are obtained at a constant current mode. Before gathering data, the STM tip is calibrated first at silver surface.

3. Computational methods and details

Our density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package (VASP) [1], where the projector augmented wave (PAW) method [2, 3] was adopted, and the generalized gradient approximation (GGA) in the framework of Perdew-Burke-Ernzerhof [4] was chosen for the exchange-correlation functional. The van der Waals (vdW) correction was treated using the DFT-D3 method [5]. The single-crystal Bi has a bilayered structure, with an ABC stacking sequence along the (111) direction [6]. The lattice constants of a hexagonal unit cell of the Bi(111) surface adopt our experimental values of a = b = 4.55 Å, and the interlayer spacing of c = 12.102 Å is ob-
obtained by our DFT optimization. The value of $c$ is in good agreement with the experimental value of Bi bulk (11.797 Å) [7], indicating that the DFT-D3 method can properly describe the vdW interactions for this system. The lattice mismatch of the Bi(111) substrate and stanene ($a = b = 4.68$ Å [8]) is 2.77%. The Bi(111) substrate was modeled by a six-bilayer slab for structural optimization and a three-bilayer slab for calculations of electronic and topological properties, both with a vacuum layer thicker than 15 Å to ensure the decoupling between neighboring slabs. A $7 \times 7 \times 1$ Monkhorst-Pack $k$-point mesh was used for the $1 \times 1$ surface unit cell. The energy cutoff was set to 400 eV in all the calculations. During the relaxation, the atoms in the bottom-most four bilayers were fixed to their respective bulk positions, while all other atoms were allowed to relax until the corresponding forces were smaller than 0.01 eV/Å. The SOC effects were considered unless otherwise specified. To investigate the topological properties in these stanene films with and without Bi(111) substrate, we calculate the $Z_2$ invariant via the Wannier charge centers [9] and construct the edge Green’s function of the semi-infinite lattice model [10] from the maximally localized Wannier functions (MLWFs) [11] as implemented in the WannierTools package [12].

The formation energy ($E_f$) of few-layer stanene on Bi(111) is defined by the formula

$$E_f = -(E_{\text{tot}} - E_{\text{sub}} - N_H \times E_H - N \times E_{\text{stanene}})/N,$$

where the $E_{\text{tot}}$, $E_{\text{sub}}$, $E_H$, and $E_{\text{stanene}}$ are the total energies of the complex system of stanene on Bi(111), the isolating Bi(111) substrate, one H atom in gas phase, and a freestanding single-layer stanene containing the same number of Sn atoms as that in one layer of stanene films, respectively, $N_H$ is the number of passivated H atoms, and $N$ is the thickness of the stanene layers. In order to examine the stability of the stanene films, we also define the second-order difference of $E_f$, by

$$E''_f(N) = -2 E_f(N) + E_f(N - 1) + E_f(N + 1).$$

If $E''_f(N) \geq 0$, the film of $N$ stanene layers is stable, otherwise the film is unstable [13].
Stacking manner between stanene layers is important for constructing the structural model and may also give an insight into the superconductivity in few-layer stanene. As mentioned in previous study [14], the superconductivity emerges in epitaxial few-layer stanene films, while it is absent in α-Sn bulk material. Thus a natural question is whether the
epitaxial few-layer stanene films possess the same stacking manner with the layered $\alpha$-Sn. To this end, we first measured the atomically resolved image at a film step to study the superposition of two stanene layers (see Fig. S2a). The derivative image gives us a clearer view for the atomic lattice, and the atomic arrays of upper sublattice Sn atoms are marked out by the red lines. Inside the film, two neighboring arrays have the same spatial distance, and each unit cell of stanene (red hexagon) occupies two times the distance. While at the longer edge, the distance between neighboring arrays is enlarged and the unit cell here is also distorted, as shown in Fig. S2a by the red distorted hexagon with an ellipse inside encircling the elongate image of Sn atom. The space ratio between these unit cells is 4:3.

We then analyzed this specific ratio and tried to simulate it using theoretical models. As shown in Fig. S2c, the top-fcc type stacking manner well reproduces the specific ratio at the A edge step. The upper sublattice Sn atoms of both the upper and lower layer stanene films are encircled by the red ellipses at the A edge, which correspond to the elongate image of Sn atoms in Fig. S2a. Considering that other stacking manners cannot give such a ratio, we confirmed that the stanene films follow the top-fcc stacking manner, namely, the configuration of $\alpha$-Sn. Therefore, the emergent superconductivity in few-layer stanene is probably caused by the compressed lattice constant.

In addition, we find morphological differences between the A and B edges. For a hexagonal film, the longer edges are the A edges, along which the cut line shows a clear atomic profile with single lattice constant; the shorter edges are B edges, along which the cut line shows an atomic profile with double lattice constants (see Fig. S2b). Origins of this dimerization at the B edges need to be further explored.
III. CONFIGURATIONS AND FORMATION ENERGIES OF STANENE FILMS ON Bi(111).

FIG. S3. Formation energies ($E_f$) of stanene on Bi(111). a, b, $E_f$ of stanene films at different layer thicknesses on Bi(111) without (a, solid symbols) and with (b, open symbols) H passivation, respectively. c, $E_f$ of the most stable configurations for different stanene thicknesses ($N = 2, 3, \ldots, 6$) without (black) and with (red) H passivation. d, The corresponding second-order differences ($E''_f$) as a function of the thickness of the stanene layers. e, Side view of atomic structure of the most stable fcc-hcp configuration of 4-layer stanene/Bi(111) with H passivation.
To gain the electronic properties of stanene films with different layer thicknesses on the Bi(111) substrate, we first explore the most stable configurations. Six possible high-symmetry configurations were considered initially, labeled by the locations of the bottom-top Sn atoms on the Bi(111) surface as fcc-hcp, fcc-top, hcp-fcc, hcp-top, top-fcc, and top-hcp. After structural optimization, we identify fcc-hcp as the most stable configuration for all the studied stanene films of layer number $N = 1, 2, \ldots, 6$ with or without H passivation. The corresponding formation energies ($E_f$) are summarized in Fig. S3a, b, and c. For the single-layer case, the fcc-hcp configuration possesses the largest $E_f$, corresponding to the lowest structural energy among all the six configurations, accounting for the better-quality stanene on Bi(111) experimentally achieved in this work due to the suppression of orientational grain boundaries [15, 16]. Furthermore, the second-order differences of the formation energies ($E'_f$) are also calculated, as shown in Fig. S3d. More strikingly, without H passivation, $E'_f(N) < 0$ with $N = 2, 3, 4,$ and $5$, indicating that the stanene films are unstable and harder to grow smoothly; in contrast, $E'_f(N) \geq 0$ for the H passivation case, indicating smooth layer-by-layer growth. Therefore, it is more favorable to grow high-quality few-layer stanene on Bi(111) with the help of hydrogen, consistent with our experimental observations, demonstrating the elegant role of hydrogen as an effective surfactant [17, 18].
FIG. S4. **Electronic structures of stanene films with different layer thicknesses on Bi (111).** a, dI/dV spectra taken on stanene films with different layer thicknesses. b, c, Calculated DOS (b) and band structures (c) of stanene films with different layer thicknesses. d, Calculated edge states of different layer stanene films.
FIG. S5. Calculated band structure of a 4-layer stanene film on Bi (111) without SOC, with different contributions of different Sn orbitals highlighted by different colors.
To visualize the distribution of edge states in both energy and space, the spatially resolved relative differences of the LDOSs (ΔLDOSs) are shown in Fig. 2e, which are acquired by the following processes: firstly, a series of dI/dV spectra across A/B edge are taken along the black arrows in Fig. 2c; secondly, all the spectra are subtracted by the spectrum taken in the interier of the island (bulk spectrum) in Fig. 2c; thirdly, the differences of the LDOS are divided by the bulk spectrum, thus we can get the spatially resolved image of ΔLDOSs which highlights the distribution of the edge states in both energy and space. A positive value of ΔLDOS at edges indicates the domination of the edge states.


