

Moiré superlattices of antimonene on a Bi(111) substrate with van Hove singularity and Rashba-type spin polarization

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Abstract

Moiré superlattices consisting of two-dimensional (2D) materials have attracted immense attention because of emergent phenomena such as flat band-induced Mott insulating states and unconventional superconductivity. However, the effects of spin-orbit coupling (SOC) on them have not been fully explored yet. Here we show that single- and double-bilayer (BL) Sb honeycomb lattices, referred to as antimonene, forms moiré superlattices on a Bi(111) substrate due to a lattice mismatch. Scanning tunnelling microscopy (STM) measurements reveal the presence of spectral peaks near the Fermi level, which are spatially modulated with the moiré period. Angle-resolved photoemission spectroscopy (ARPES) combined with density functional theory (DFT) calculations clarifies the surface band structure with saddle points near the Fermi level, which allows us to attribute the observed STM spectral peaks to the van Hove singularity. Spin-resolved ARPES measurements also shows that the observed surface states are Rashba-type spin-polarized. The present work has significant implications that Fermi surface instability and symmetry breaking may emerge at low temperatures, where spin degree of freedom and electron correlation will also play important roles.

The advent of artificially stacked two-dimensional (2D) materials with moiré superlattices, which are induced by a lattice mismatch and/or a twist angle, has brought a new paradigm in condensed matter physics and materials science¹⁻³. The successful fabrications of graphene/hexagonal boron nitride heterostructures and, more recently, twisted double layers of graphene have spawned a series of exciting discoveries, e.g., Hofstadter’s butterfly and fractal quantum Hall effect⁴⁻⁶, correlated insulating states and unconventional superconductivity⁷⁻⁹, charge order¹⁰, ferromagnetism and quantum anomalous Hall effect¹¹⁻¹⁴. Introduction of spin-orbit coupling (SOC) into moiré superlattices can lead to even richer emergent phenomena such as topological superconductivity, but these studies have been limited to transition metal dichalcogenides so far¹⁴⁻¹⁸. Application of elemental 2D materials with strong SOC may greatly expand the potential of moiré superlattices, but the exploration of such a possibility has been scarce so far¹⁹.

Bi and Sb are heavy VA elements with strong atomistic SOC and hence important ingredients of topological materials. As the most stable form of bulk crystals, they take the A7 rhombohedral crystal structure and consist of covalently-bonded buckled honeycomb 2D layers (conventionally called “bilayer”) stacked by weak interlayer bonding²⁰⁻²². This feature makes Bi and Sb atomic layers promising 2D materials beyond graphene²³⁻²⁵. They were theoretically predicted to become 2D topological insulators (quantum spin Hall insulators) and their topological edge states were found experimentally²⁶⁻³². They are also reported to be resilient against air exposure and chemical processes, and thus can be potentially used for various practical applications^{23,24,33}.

Here we show using scanning tunnelling microscopy (STM) that single- and double-bilayer (BL) Sb honeycomb lattices, referred to as antimonene^{23,25,34-38}, forms moiré superlattices on a Bi(111) substrate due to a lattice mismatch. They exhibit clear spectral peaks located near the Fermi level, which show distinctive behaviours regarding the moiré periodicity. While the peaks found for the single-BL antimonene shows only weak modulations in height, those for the double-BL antimonene are split by ~100 mV and exhibit strong spatial modulations, suggesting the localization due to the moiré superlattice. Angle-resolved photoemission spectroscopy (ARPES) and spin-resolved ARPES (SARPES) combined with density functional theory (DFT) calculations clarify the presence of saddle points near the Fermi level. This allows us to identify the origin of the STM spectral peaks as the van Hove singularity. These surface states are found to be Rashba-type spin-polarized. The present work has significant implications that Fermi surface instability and symmetry breaking may emerge at low temperatures, where spin degree of freedom and electron correlation are intimately involved.

Results

All experiments were carried out in ultrahigh vacuum (UHV) chambers with the base pressure of $\sim 1 \times 10^{-10}$ mbar (see Methods). First, a Bi(111) thin film was grown to 10 BL by molecular beam

epitaxy (MBE) on a clean Si(111) surface^{39,40}. For some of the ARPES experiments, a 250 BL-thick Bi(111) film was grown on a clean Ge(111) surface^{41,42}. Here we adopt the rhombohedral crystallographic notation to describe the plane index of the film^{20,21}. The crystallinity of prepared samples were confirmed with STM and low energy electron diffraction (LEED). The surface of the Bi(111) film was then covered by 1-2 BL Sb (for LEED patterns, see Supplementary Information A). Since Bi(111) and Sb(111) bilayers share the same buckled honeycomb structure with close lattice constants of 0.454 nm and 0.431 nm, respectively, a Sb(111) film could grow epitaxially on a Bi(111) film^{43,44}. However, the lattice constant of the free-standing Sb bilayer (1BL antimonene), predicted to be 0.408-0.412 nm^{45,46}, is significantly smaller than that of bulk Bi(111). This allows antimonene to grow non-epitaxially on Bi(111) and to form a moiré superlattice, which we indeed observe as follows.

The main panel of Fig. 1a shows a representative STM image of a Bi(111) surface covered with more than 1 BL of Sb. The lower terrace in the image (Region I) features a triangular lattice structure, which is a moiré superlattice made of a 1BL antimonene (1BL Sb) on a Bi(111) surface. Although this superlattice includes defects and local deformations, the presence of a well-defined periodicity is clear from its fast Fourier transformed (FFT) image (Inset of Fig. 1a). From repeated experiments with different surface regions and samples, we have determined the moiré lattice constant to be 4.70 ± 0.30 nm (Supplementary Information B). On the upper terrace, there exists another region of moiré superlattice with a longer periodicity (Region II). Since the height difference of ~ 0.4 nm between Regions I and II (Fig. 1b) is approximately equal to the height of Sb bilayer (0.374 nm for bulk)²⁰, Region II is identified as 2BL antimonene (2BL Sb) on a Bi(111) surface. Its moiré lattice constant was determined to be 6.59 ± 0.89 nm. The relatively large uncertainty is due to variations throughout different surface regions, presumably reflecting very small energy differences caused by them. This 2BL Sb is bordered with another 1BL Sb layer (Region III) located on the upper-right corner of the image. Since they have almost the same topographic heights²⁰, the boundary (indicated by the dashed line) is identified as the location of a buried atomic step of Bi(111) surface. Our repeated experiments indicate that antimonene layers grow from the step edges of Bi(111) surfaces (Supplementary Information C).

Magnified STM images of 1BL and 2BL Sb are displayed in Fig. 1c and Fig. 1d, respectively, where the Sb atomic lattices are clearly resolved. The moiré unit cells are indicated by the dashed parallelograms. We determined the lattice constant of 1BL Sb to be 0.415 ± 0.004 nm (Supplementary Information B). The fact that this value is larger than that of free antimonene (0.408-0.412 nm)^{45,46} is attributed to the tensile strain exerted from the Bi(111) surface. Likewise, the lattice constant of 2BL Sb was determined to be 0.423 ± 0.005 nm. This value is closer to that of bulk Sb(111) (0.431 nm) than that of 1BL Sb, suggesting a lattice relaxation toward the bulk crystal. Combined with the moiré lattice constant determined above, the ratio of the numbers of

Bi and Sb atoms can be calculated. We find $(N_{\text{Bi}} : N_{\text{Sb}}) = (10 : 11)$ for 1BL Sb and $(N_{\text{Bi}} : N_{\text{Sb}}) = (13 : 14) - (17 : 18)$ for 2BL Sb, where N_{Bi} and N_{Sb} are the number of Bi and Sb atoms within the unit cells along the principal axis. Our FFT analysis of STM images over an extended area reveals that there is no twisting between of the moiré and Sb lattices on average (Supplementary Information B), although there are some local deviations due to deformations. Furthermore, Fig. 1c, d shows that the surface is divided into three characteristic regions in terms of topographic height. By comparing this observation to previous reports on related moiré superstructures⁴⁷⁻⁵¹, we can safely assign them to the regions of AA, AB, and AC stacking sequences (Fig. 1e). In the AA stacking, all atoms in the two layers are vertically overlapped, while only half of them are in the AB and AC stackings. Because of the significant buckling of the honeycomb lattice, the vertical distance between the overlapped atoms in the AB stacking is larger than in the AA stacking. This leads to the lowering of the top layer by an attractive force. Conversely, in the AC stacking, the vertical distance between the overlapped atoms is smaller than that of the AA stacking. This leads to the raising of the top layer by a repulsive force. As a result of structural relaxations, the areas corresponding to the AB and AC stacking regions expand and shrink, respectively^{47,48}. These features are clearly observed in Fig. 1c, d.

The electronic states of the moiré superlattices and their spatial modulations were investigated by scanning tunnelling spectroscopy (STS). First, for 1BL Sb on Bi(111), dI/dV spectra were taken at the centre of the AA stacking region up to five locations, and this process was repeated for the AB and AC stackings. The selected spectral sites are shown in the topographic STM image in Fig. 2a with red (AA), blue (AB), and green (AC) squares. Figure 2b shows the results of the STS measurements. The broken lines show individual dI/dV spectra and the solid lines their averages for the same stacking sequences, with their colours corresponding to those in Fig. 2a. The average of all measured spectra are also shown by the solid black line. For all of these spectra, clear peak structures are noticeable near the zero bias voltage, with the full width at half maximum of 80 – 100 mV. The spectral peaks at the AB sites are particularly conspicuous, while those at the AA and AC sites are relatively suppressed. More detailed information was obtained through a line spectroscopy measurement; dI/dV spectra were taken along a straight line connecting the centres of AC, AB, AA, and AC sites in this sequence. The right panel of Fig. 2c shows a 2D plot of colour-coded dI/dV spectra as a function of bias voltage and lateral distance from the starting point. In the left panel of Fig. 2c, the topographic profile along the line is also shown. We find that the spectral peak is fixed around 0 – 30 mV, while its intensity is varied. The result strongly suggests the presence of delocalized states around the Fermi level that are weakly modulated by the moiré superlattice.

Figure 2d-f displays site-dependent dI/dV spectra for 2BL Sb on Bi(111) obtained in the same manner. The symbols and colours used in the figure follow the convention in Fig. 2a-c. Figure 2e

shows that spectral peaks are shifted from the zero bias by 48 mV (AA site), -48 mV (AB site), and 144 mV (AC site) on average. The right panel of Fig. 2f shows that clear peak structures around 40 mV and -100 mV are confined within the AA and AB regions, respectively. The result indicates the presence of multiple states near the Fermi level that are localized due to the moiré superlattice⁵².

To clarify the origin of the spectral peaks observed by STS, we performed laser-based high-resolution ARPES/SARPES measurements⁵³. For simplicity, the data were analysed based on the Brillouin zone of Bi(111) (Fig. 3a). First, we focus on the result of 1BL Sb on a Bi(111) surface. Figure 3b shows a 2D plot of ARPES intensity along the Γ -M direction and as a function of binding energy E_B (dark: high, bright: low). We can recognize two bands denoted as S_1 and S_2 starting from $E_B \cong 0.2$ eV and dispersing upward. These bands disappear around $k_x = 0.05 - 0.1 \text{ \AA}^{-1}$ by crossing the Fermi level but seem to disperse downward and appear again around $k_x = 0.4 - 0.5 \text{ \AA}^{-1}$. The band dispersions determined from the plot are highlighted with the red dashed curves. They are better visualized by SARPES signal plotted for the range of $-0.22 \text{ \AA}^{-1} < k_x < +0.22 \text{ \AA}^{-1}$, where the intensity and the spin polarization in the y direction are indicated by brightness (dark: high, bright: low) and colour (red: positive, blue: negative), respectively. The maximum spin polarization of photoelectron amounts to ~ 0.6 . The spin polarizations of the S_1 and S_2 bands are opposite to each other and are antisymmetric with respect to $k_x = 0 \text{ \AA}^{-1}$. This is characteristic of Rashba-type spin-polarization, which will be discussed later. Figure 3c shows a similar 2D plot of ARPES intensity along the $\bar{\Gamma} - \bar{K}$ (k_y) direction. The S_1 and S_2 bands are also noticeable (highlighted with the red dashed lines), but the S_2 band reaches the local maximum near the Fermi level around $k_y = 0.1 \text{ \AA}^{-1}$ and then disperses downward.

Figure 3e shows the 2D plot of ARPES intensity measured near the Fermi level ($E_B = 0.02$ eV) in the $k_x - k_y$ space, which gives the Fermi surface contour. The central ring and a surrounding star-like structure are clearly noticeable, which can be identified as the S_1 and S_2 bands, respectively. We note that some parts of the S_2 band appear very weak due to the anisotropic transfer matrix element in the photoemission process. By referring to the band dispersions in Fig. 3b-d, we can identify the areas indicated by the red ellipsoids as saddle points, where the S_2 band takes a local maximum in the $\bar{\Gamma} - \bar{K}$ direction and a local minimum in the orthogonal direction. This means that the van Hove singularity exists at the Fermi level⁵⁴ and explains the origin of the zero bias peak for 1BL Sb/Bi(111) described above. To confirm this result, we also performed a Fermi surface mapping with an imaging-type ARPES instrument, which allows us to access a larger momentum space with a faster speed (Fig. 3f)⁴². The acquired Fermi surface well reproduces the features observed in Fig. 3e, while better reflecting the six-fold symmetry expected from the C_3 and time-reversal symmetries of the present system. We note that the band structure and the Fermi surface resemble those of Bi(111) and Sb(111) surfaces^{21,40,41,55,56}, while saddle

points are absent near the Fermi level in the latter cases.

The distribution of spin polarization in the momentum space was investigated with the same imaging-type instrument for 1BL Sb/Bi(111). Figure 3g shows a 2D plot of SARPES intensity and spin polarization in the y direction (P_y) measured near the Fermi level ($E_B = 0.03$ eV). The observed signal is mostly attributed to the S_2 band, the location of which is reproduced from the Fig. 3f (red solid lines). Along the k_x axis (white dashed line), the distribution of P_y signal is antisymmetric with respect to $k_y = 0$. This is consistent with a Rashba-type spin polarization as mentioned above. We should note that the actual distribution of spin polarization is deviated from the ideal vortical form, as indicated by the reversal of P_y with respect to the lines at $\pm 60^\circ$ to the k_x axis (black dashed lines). An analogous behaviour was also predicted and observed for a clean Bi(111) surface with a giant Rashba-splitting^{42,57,58}.

We also performed ARPES/SARPES measurements of 2BL Sb on a Bi(111) surface (Supplementary Information D). The results are nearly identical to those of 1BL Sb/Bi(111) (Fig. 3), but the observed ARPES signals are clearer than those of 1BL Sb/Bi(111). This may be attributed to the better moiré periodicity observed with STM (Fig. 1a).

The *ab initio* calculations of the electronic structure of the Sb/Bi(111) moiré superlattices is difficult because of a huge number of heavy atoms involved within a moiré unit cell. To circumvent this problem, we carried out DFT calculations based on an epitaxial model consisting of 1BL Sb(111) on 5BL Bi(111) (Methods). Although this model does not include the effect of moiré periodicity, it can account for the overall band structures within the Bi(111) Brillouin zone. The structural relaxation within each stacking region in the actual moiré structure (Fig. 1c,d) rationalizes this treatment. Figure 4a shows the band diagrams calculated for the AB stacking sequence. The orange and blue rectangles correspond to the same marked areas in Fig. 3b,c. The sizes of the purple (light blue) circles represent the contributions of the top Sb (Bi) BL. Among all, the two bands starting from the $\bar{\Gamma}$ point below the Fermi level (designated by the red dashed lines) are mostly derived from the top Sb BL, indicating that they can be preferentially detected in the surface-sensitive STM and ARPES measurements. Judging from their dispersions, they can be assigned to the S_1 and S_2 bands identified above (Fig. 3b-d). The same calculations for the AA and AC stackings give very similar band structures near the $\bar{\Gamma}$ point and around the Fermi level (Supplementary Information E, Fig. E1). Therefore, the presence of saddle points near the Fermi level is theoretically confirmed. These features are reflected in the projected density of states (PDOS) on the top Sb BL (Fig. 4c). The three sharp peaks indicated by the arrows at $E - E_F = 0.02 - 0.05$ eV, corresponding to the AA, AB and AC stackings, are due to the van Hove singularity of the saddle point. The peak energies are very close to one another, reproducing the STS results of Fig. 2b,c. Assuming that the Fermi level is aligned near these peaks in real samples, we plot the Fermi surface contour of 1BL Sb(111)/ 5BL Bi(111) with the AB stacking at $E - E_F$

= -0.02 eV (Fig. 4b). The central rings and a surrounding star-like structure are consistent with the ARPES result (Fig. 3e, f).

The same calculations were also conducted based on an epitaxial model of 2BL Sb(111) on 5BL Bi(111). The band structures and the Fermi surface ($E - E_F = -0.02$ eV) obtained for the AB stacking (Fig. 4d, e) resemble those for the 1BL Sb(111) model (Fig. 4a, c) as well as ARPES results (Supplementary Information D). This is also the case for the AA and AC stackings (Supplementary Information E, Fig. E2). However, the PDOS around the Fermi level calculated for the AA, AB, AC stackings exhibit at more separated energies (Fig. 4f). Qualitatively, the result is in line with the STS data (Fig. 2e, f), but there exists some clear discrepancies; e.g., the sharp peak at $E - E_F = 0$ eV for the AC stacking has no corresponding structure in the STS data (Fig. 2e). This may be attributed to an incomplete structural optimization for the 2BL Sb model, which results from our simplified models of fixing the locations of the Bi atom to those of bulk Bi crystal (see Methods).

Discussion

We have calculated the band structures of antimonene on a Bi(111) surface based on epitaxial models of 1BL Sb(111)/5BL Bi(111) and 2BL Sb(111)/5BL Bi(111), which successfully explains our STM and ARPES data. Obviously, the adopted models are rather crude and do not include the effects of moiré modulations. The fact that all stacking sequences AA, AB, and AC result in qualitatively same electronic band structures may also explain the success of the present models. We also note that Bi is a topologically non-trivial semimetal and its (111) surface states are protected⁴¹. Since Sb and Bi are isovalent, the surface states of antimonene on Bi(111) can be topologically equivalent to those of Bi(111). The absence of energy gaps due to the moiré superlattice, at least within the experimental resolution, may be due to the topological protection against potential modulations. In this case, (high-order) van Hove singularities are predicted to emerge at the \bar{K} point of the moiré Brillouin zone⁵⁹, which calls for a future study.

Finally, we discuss the implications of the findings in the present work. Generally speaking, the presence of the van Hove singularity means a logarithmic divergence of density of states and an enhancement of Coulomb interactions. The tuning of the Fermi level to a van Hove singularity point can lead to a variety of the symmetry-broken phases at low temperatures such as unconventional superconductivity, charge density wave, ferromagnetism, charge order, and nematicity, which have been discussed within the context of high- T_c cuprates, graphene, kagome metals, etc^{54,60-63}. Since the van Hove singularities in our systems is located close to the Fermi level, their tuning must be technically viable through gate voltage or molecular doping⁶⁴. Among the possible low-temperature phases, superconductivity is the most likely because the presence of Rashba-type spin polarization and the resulting spin-momentum locking⁵⁹. In this case, the

absence of space inversion symmetry should lead to a spin singlet-triplet mixed state⁶⁵. We note that an electron-phonon coupling, responsible for superconductivity, is likely to be enhanced here as discussed for granular Bi films^{66,67}. Regarding 2BL Sb/Bi(111), moiré-induced electron confinement and enhanced electron correlation can further enrich the low-temperature physics beyond the simple van Hove singularity scenario. The inclusion of Rashba-type spin polarization into the moiré system is an open and intriguing problem. Thus, the present Sb/Bi(111) moiré superlattices will offer a new playground to investigate the role of spin degree of freedom in van der Waals materials.

Methods

Sample preparation

Si(111) substrates were cleaned by direct current heating at 1250°C for 10 seconds. After repetition of the cycle several times, clean 7×7 surfaces were obtained. Ge(111) substrates were cleaned by repetition of Ar⁺ sputtering and annealing several times to obtain 2×1 surfaces. Both surfaces were confirmed by observing sharp LEED spots. Bi(111) films were then grown by MBE on Si(111)-7×7 surfaces to 10 BL or on Ge(111)-2×1 surfaces to 250 BL at the room temperature. To improve the flatness of the film, the Bi films was annealed around 190°C for 5 min. Subsequently, Sb was deposited on Bi(111) surfaces at the room temperature to form moiré antimonene. The crystallinity of the sample was improved by a mild annealing around 100 °C.

STM measurements

The STM measurements were conducted at 78 K and 4.6 K with a Nanonis controller Mimea BP5e. Topographic images were obtained in the constant current mode. The lateral scale of STM images was calibrated through observation of Bi(111) surfaces by assuming that the lattice constant is equivalent to that of a bulk crystal (0.454 nm). STS measurements were conducted with a built-in lock-in amplifier with a typical bias voltage modulation of 20 mV at 477 Hz.

ARPES measurements

ARPES and SARPES measurements were performed at National Institute for Materials Science (NIMS) and at the Institute for Solid State Physics (ISSP), The University of Tokyo. For the measurements at NIMS, we employed a momentum microscope equipped with an imaging spin detector^{42,68}. A 10.9-eV laser was used as the excitation light. For the measurements at ISSP, the photoelectrons excited by a 6.994-eV laser were analysed by a hemispherical photoelectron analyser equipped with an ultra-low-speed electron diffraction spin detector⁵³. For both measurements, samples were *in situ* prepared. The sample temperature during the measurements was 30 K.

DFT calculations

To calculate the electronic band structures, we adopted epitaxial models of 1BL Sb(111)/ 5BL Bi(111) and 2BL Sb(111)/ 5BL Bi(111). The locations of the Bi atoms and those of the Sb atoms in the in-plane directions were fixed to those of bulk Bi crystal. The out-of-plane Bi atom positions follow the structure for the Bi(111) thin film used in the literature⁶⁹. Here, the Bi atom locations in the top Bi BL (adjacent to the Sb BLs) are modified while other Bi atoms follow the bulk Bi structure. By contrast, the locations of the Sb atoms in the out-of-plane direction were set equal to those at the centres of the AA, AB and AC stacking region of numerically optimized moiré

superlattices (indicated by the red, blue and green circles, respectively, in Fig. E1a and Fig. E2a; see Supplementary Information E). To optimize the 1BL Sb(111)/ 5BL Bi(111), we prepared a single 11×11 supercell of the Sb(111) BL on five vertically stacked 10×10 supercells of the Bi(111) BL. While the locations of the Bi atoms are fixed as same as in the Bi(111) thin film⁶⁹, the locations of the Sb atoms are optimized by utilizing a neural network potential, PFP (without U) version 5.0.0 on Matlantis (<https://matlantis.com/>)⁷⁰. Similarly, to optimize the 2BL Sb(111)/ 5BL Bi(111), we prepared two 14×14 supercells of the Sb BL on five 13×13 supercells of the Bi BL, and optimized the positions of the Sb atoms.

The non-collinear DFT calculations for the epitaxial models are performed by OpenMX version 3.9⁷¹⁻⁷⁴ with the PBE exchange correlation functional and spin-orbit coupling. We use the $15\times 15\times 1$ k-point grid in the first Brillouin zone for the self-consistent field (SCF) calculations. After the SCF calculation, the density of states is obtained on the $256\times 256\times 1$ k-point grid by the tetrahedron method. The energy cutoff is set to be 100 or 200 Ry. The dependence of the band structure and density of states on the k-point grid and energy cutoff has been examined to ensure convergence.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Author contributions

T.N. and T.U. conceived the experiment and T.N., T.U., K.Y. and Y.Y. wrote the manuscript. T.N., R.N. and Q.W. carried out the STM measurements and T.N. analysed the data. T.N., K.Y., Y.F., K.K., R.M. carried out (S)ARPES measurements at ISSS under supervision of T.K. Y.C., K.Y., and S.T. carried out (S)ARPES measurements at NIMS. K.Y. and S.T. analysed the ARPES/SARPES data. Y.Y. performed the DFT calculations. All the authors discussed the results and contributed to finalising the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information

The supplementary materials A-E are available online. Correspondence and requests for materials should be addressed to T. Uchihashi.

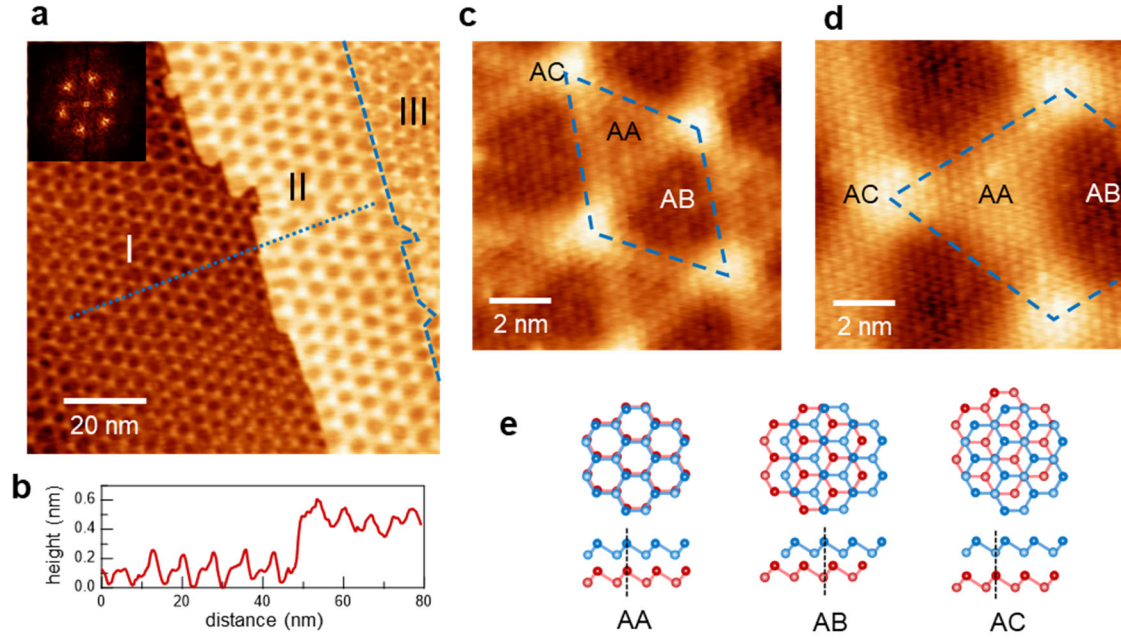


Fig. 1 | Topographies and atomic structures of antimonene/Bi(111) moiré superlattices. **a** STM topographic image of 1BL and 2BL Sb grown on a Bi(111) film (Sample bias voltage: $V_s = -1.0$ V, Tunnelling current: $I_t = 100$ pA). Regions I and III correspond to 1BL Sb while Region II to 2BL Sb. The inset shows a FFT transform of a surface area belonging to Region I. **b** Height profile along the dotted line in **a**. **c**, **d** Atomic resolution images of 1BL Sb (**c**) and 2BL Sb (**d**) on a Bi(111) surface. ($V_s = -50$ mV, $I_t = 500$ pA (**c**), $V_s = -50$ mV, $I_t = 300$ pA (**d**)). The dashed parallelograms indicate the unit cells of the moiré superlattices. **e** The top and side views of the AA, AB and AC stacking sequences (blue spheres: Sb, red spheres: Bi). The vertical dashed lines shows the alignment of the Sb and Bi atoms.

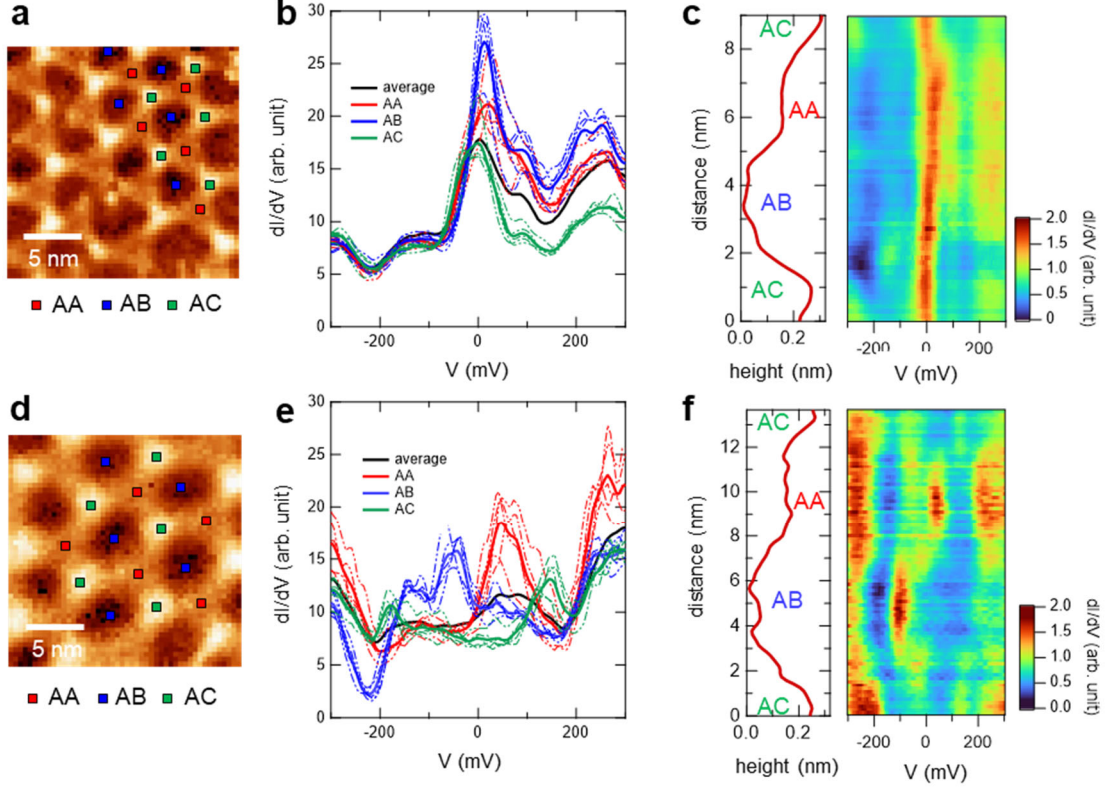


Fig. 2 | Local electronic structures of antimonene/Bi(111) moiré superlattices near the Fermi level. **a** STM topographic image of 1BL Sb/Bi(111) moiré superlattices ($V_s = -300$ mV, $I_t = 100$ pA). The red (AA), blue (AB), and green (AC) squares show the locations for the STS measurements. **b** dI/dV spectra obtained at individual locations shown in **a** (broken lines) and their averages (solid lines) taken for the same stacking sequences. The red, blue, and green lines correspond to AA, AB, and AC stackings, respectively. The black solid line is the average of all the spectra. **c** (Right panel) 2D plot of colour-coded dI/dV spectra of 1BL Sb/Bi(111) moiré superlattices, which was taken along a straight line connecting the centres of AC, AB, AA, and AC regions. The vertical axis represents the lateral distance from the starting point. (Left panel) Topographic cross section along the measurement line. **d**, **e**, **f** Results for 2BL Sb/Bi(111) moiré superlattices obtained in the same manner as in **a**, **b**, **c**.

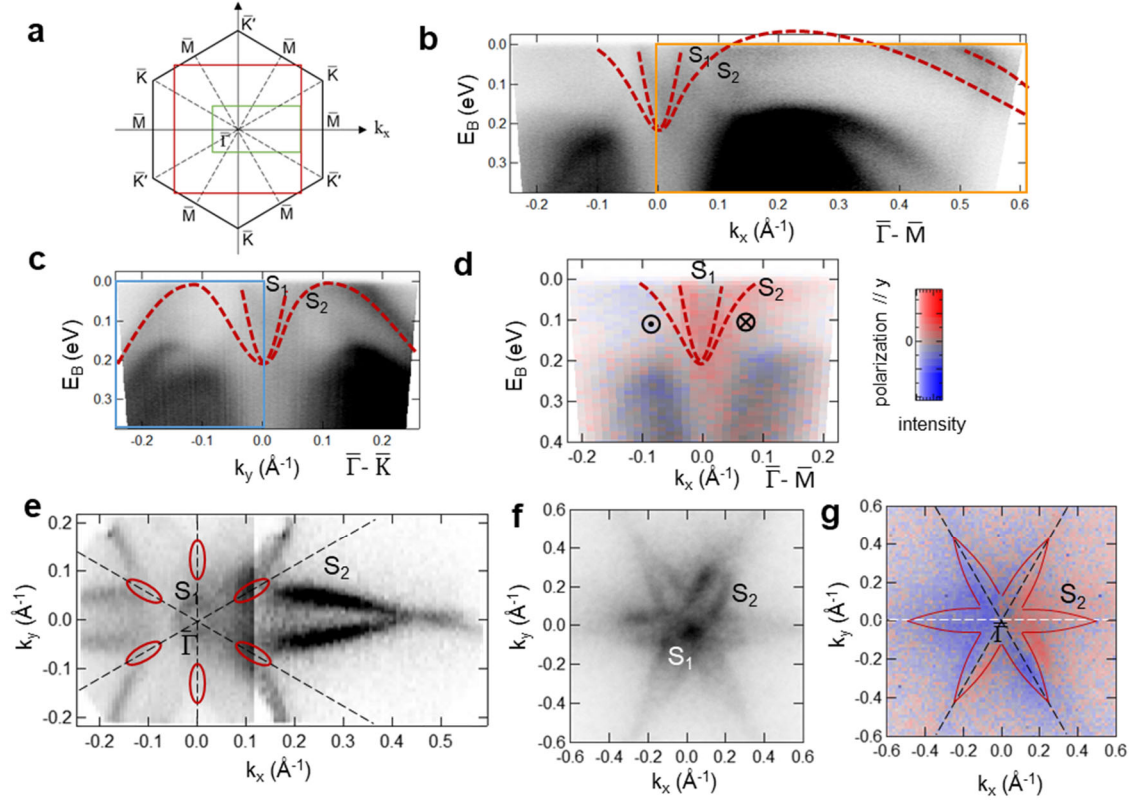


Fig. 3 | Electronic and spin structures of 1BL antimonene/Bi(111) moiré superlattices in the momentum space. **a** Bi(111) Brillouin zone and the high symmetry points $\bar{\Gamma}$, \bar{M} , \bar{K} , \bar{K}' . The green rectangle and the red square correspond to the areas for **e** and **f, g**, respectively. **b** 2D plot of ARPES intensity as a function of momentum k_x along the $\bar{\Gamma} - \bar{M}$ direction and as a binding energy E_B . **c** The same plot as in **b** along the $\bar{\Gamma} - \bar{K}$ direction. The orange and blue rectangles correspond to those shown in Fig. 4a. **d** 2D plot of the SARPES signal as a function of momentum k_x along the $\bar{\Gamma} - \bar{M}$ direction and as a binding energy E_B . The intensity and the spin polarization in the y direction are indicated by brightness (dark: high, bright: low) and colour (red: positive, blue: negative), respectively. In **b-d**, the dispersions of S_1 and S_2 bands are indicated by the red dashed lines. **e** 2D plot of ARPES intensity measured near the Fermi level ($E_B = 0.02$ eV) in the $k_x - k_y$ space, which gives the Fermi surface contour. The plot includes two data sets obtained in separate runs, which causes an apparent discontinuity at $k_x = 0.12 \text{ \AA}^{-1}$. The dashed lines indicate the $\bar{\Gamma} - \bar{K}$ directions. The red ellipsoids show the locations of the saddle points of the S_2 band. **f** The same plot as in **e** in a larger momentum space, which was obtained with the imaging-type instrument. **g** 2D plot of SARPES intensity and spin polarization in the y direction measured near the Fermi level ($E_B = 0.03$ eV) obtained with the imaging-type instrument. The intensity and the spin polarization in the y direction are plotted as in **d**. The Fermi surface contour of the S_2 band determined from **f** is shown with red solid lines. The black and white dashed lines indicate the $\bar{\Gamma} - \bar{M}$ directions.

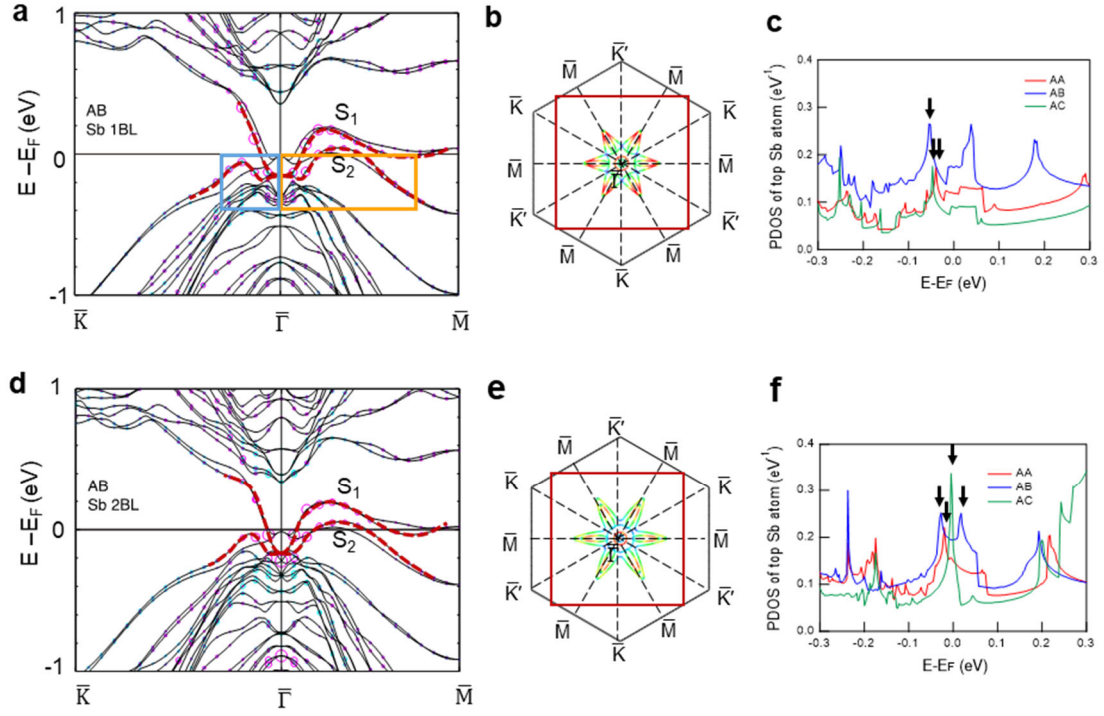


Fig. 4 | DFT band structure calculations for the Sb(111)/ Bi(111) epitaxial models. **a, d** Band dispersions along the $\bar{K} - \bar{\Gamma} - \bar{M}$ direction calculated with the 1BL Sb(111)/5BL Bi(111) model (**a**) and the 2BL Sb(111)/5BL Bi(111) model (**d**) with AB stacking. The orange and blue rectangles correspond to those shown in Figs. 3b and 3c. The sizes of the purple (light blue) circles represent the contributions of the top Sb (Bi) BL. **b, e** Fermi surfaces ($E - E_F = -0.02$ eV) calculated for the 1BL Sb(111)/5BL Bi(111) model (**b**) and the 2BL Sb(111)/5BL Bi(111) model (**e**). The colours represent the Fermi velocity (red: fast, blue: slow). The red squares correspond to the regions displayed in Fig. 3f, g. **c, f** Projected density of states (PDOS) on the top Sb BL density of states (DOS) calculated for the 1BL Sb(111)/5BL Bi(111) model (**c**) and the 2BL Sb(111)/5BL Bi(111) model (**f**).

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Supplementary Information for “Moiré superlattices of antimonene on a Bi(111) substrate with van Hove singularity and Rashba-type spin polarization”

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- D. ARPES/SARPES measurements of 2BL antimonene on a Bi(111) surface
- E. DFT band structure calculations for the epitaxial Sb(111)/Bi(111) models

A. LEED patterns of antimonene on Bi(111) surfaces

LEED measurements were conducted for Bi(111) surfaces before and after deposition of Sb at room temperature (before: Fig. A1a, after: Fig. A1b-f). First, the deposition of Sb induces fine features around the principal LEED spots of Bi(111) (Fig. A1b-d), which are attributed to the moiré superlattices of 1BL antimonene. Increase in deposition time results in formation of broader spots (Figure A1e,f). The deposition time was converted to the Sb coverage through STM imaging of the prepared samples. Figure A1c (30 min deposition) corresponds to the coverage of 1.0 BL Sb.

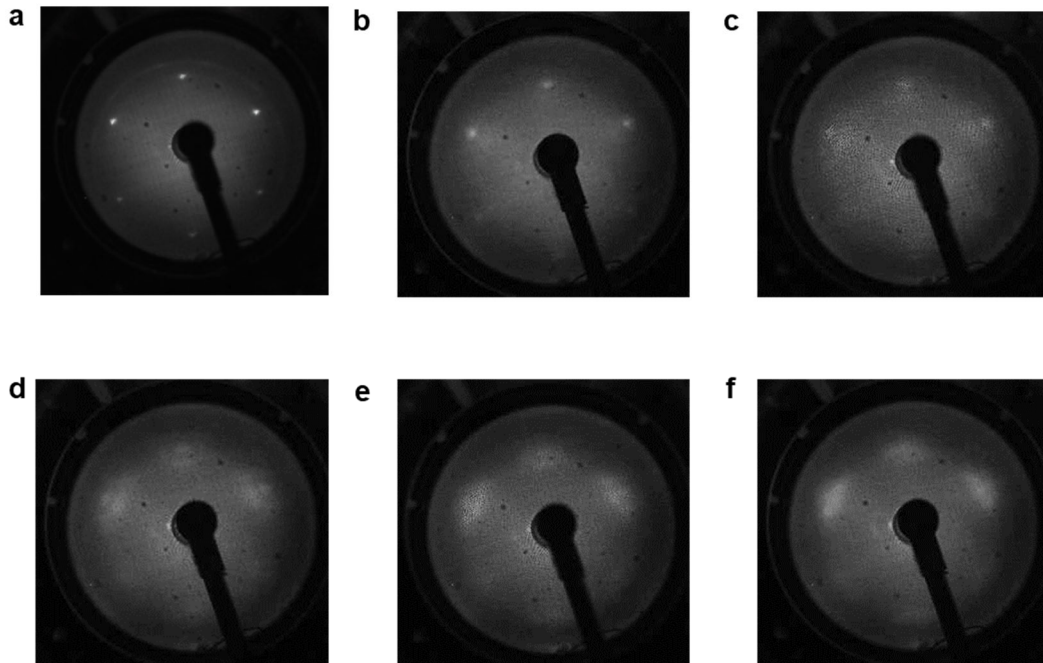


Fig. A1 | LEED patterns of Sb on Bi(111) surfaces. **a** Bi(111) clean surface. **b-f** Bi(111) surfaces after deposition of Sb for 20 min (0.67 BL Sb) (**b**), 30 min (1.0 BL Sb) (**c**), 40 min (1.33 BL Sb) (**d**), 50 min (1.67 BL Sb) (**e**), 60 min (2.0 BL Sb) (**f**). The beam energy was set at 46.5 eV.

B. Determination of the atomic structures of antimonene on Bi(111) and the moiré superlattices

To determine the lattice constant of Sb layers on Bi(111) and the moiré periodicities, fast Fourier transform (FFT) images (Fig. B1b, c, e, f) are taken from topographic image of 1BL Sb on Bi(111) (Fig. B1a) and 2BL Sb on Bi(111) (Fig. B1d). Two kinds of spots with the hexagonal symmetry are shown in FFT images. These spots are consistent with the Sb(111) surface and the moiré superlattice in topographic image. The outer spots indicated by yellow circles (Fig. B1b,e) correspond to the atomic lattice of Sb, while the inner spots indicated by red arrows (Fig. B1c, f) to the moiré superlattice. They are aligned in the same directions, revealing that there is no twisting between the Sb and Bi atomic layers. The lattice constant of the Sb lattice and the moiré period were calculated from the distance between the spots in FFT image. Our repeated experiments lead to a lattice constant of 0.415 ± 0.004 (0.423 ± 0.005) nm for the 1BL (2BL) Sb lattice. The moiré periodicity is 4.70 ± 0.30 (6.59 ± 0.89) nm for 1BL (2BL) Sb. The STM images were calibrated by assuming that the lattice constant of a 10BL Bi(111) clean surface is equal to that of a bulk crystal (0.454 nm).

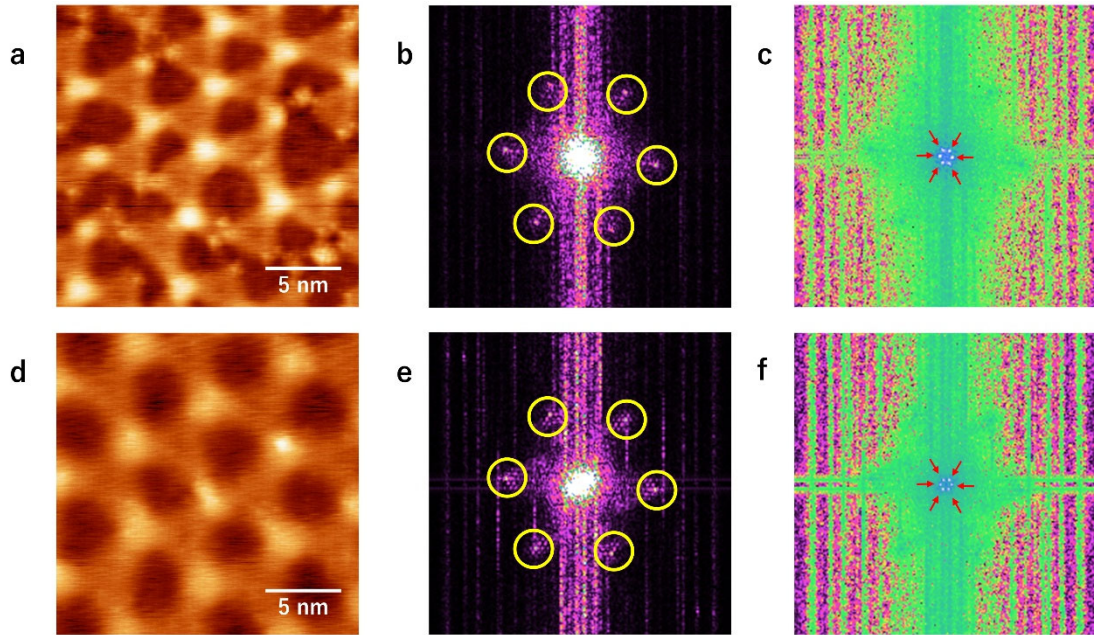


Fig. B1 | STM images of antimonene on Bi(111) and their FFT analysis. **a, d** STM topographic images of 1BL (**a**) and 2BL Sb (**d**) grown on a Bi(111) film (Sample bias voltage: $V_s = 10$ mV, Tunnelling current: $I_t = 300$ pA). **b, e** Fast Fourier transform images of **a** and **d**. The spots indicated by the yellow circles correspond to the atomic lattice of Sb. **c, f** Fast Fourier transform images of **a** and **d** displayed with a different colour scale. The spots indicated by the red arrows correspond to the moiré superstructures.

C. Growth behaviour of antimonene

A Bi(111) film was grown by MBE on Si(111)-7×7 surfaces to 10 BL at the room temperature. To improve the flatness of the film, the Bi films was annealed around 190 °C for 5 min. A STM image shows flat Bi(111) terraces with step edge running along the three-fold crystallographic orientations (Fig. C1a). Subsequently, Sb was deposited on Bi(111) surfaces at the room temperature to form moiré antimonene. The first layer of antimonene was found to grow from step edges of Bi(111) surfaces toward to the lower side of the step, while the second layer of antimonene from those of the first layer (Fig. C1b, c). These observations indicate a step-flow growth mechanism of antimonene.

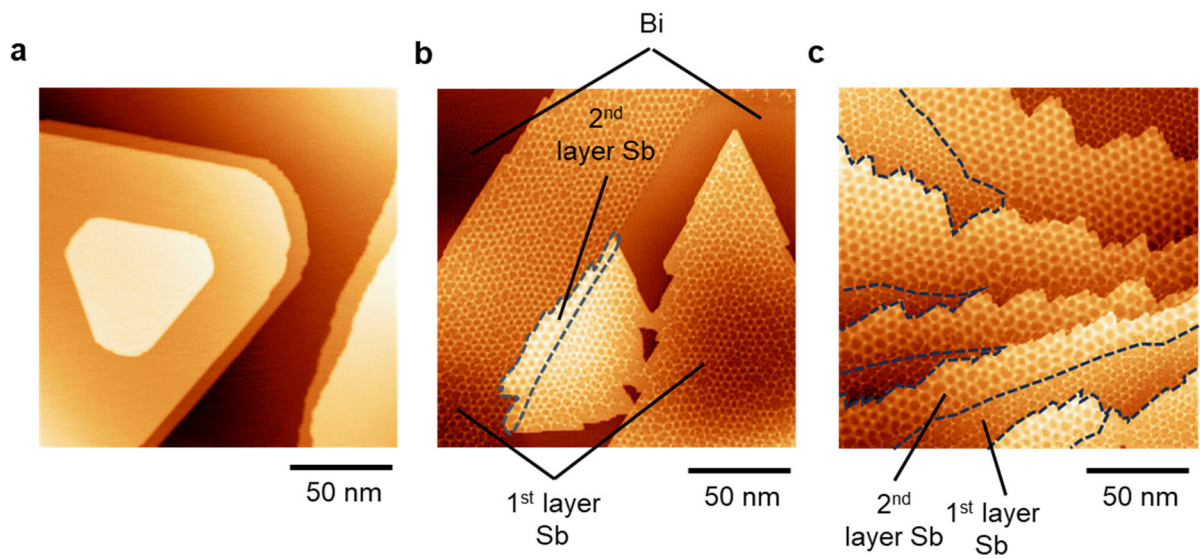


Fig. C1 | Growth behaviour of antimonene on a Bi(111) surface. **a** Topographic STM images of 10 BL Bi(111) on Si(111). **b, c** Topographic STM images of 10 BL Bi(111) on Si(111) after deposition of 0.8 BL Sb (**b**) and 1.5 BL Sb (**c**).

D. ARPES/SARPES measurements of 2BL antimonene on a Bi(111) surface

We performed ARPES/SARPES measurements of 2BL Sb on a Bi(111) surface. The results are nearly identical to those of 1BL Sb/Bi(111) (Fig. 3b, d, e); the S_1 and S_2 bands dispersing from the $\bar{\Gamma}$ point similarly (Fig. D1a), Rashba-type spin polarisation (Fig. D1b), and saddle points on the Fermi surface along the $\bar{\Gamma} - \bar{K}$ direction (the red ellipsoids in Fig. D1c). The van Hove singularity of the saddle points also explains the dI/dV spectral peaks observed for 2BL Sb/Bi(111) (Fig. 2e).

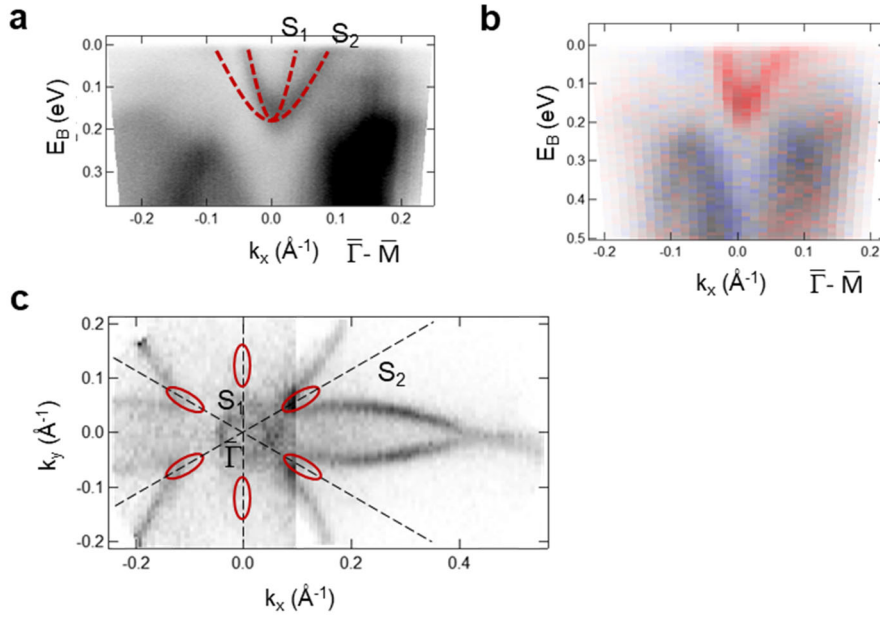


Fig. D1 | Electronic and spin structures of 2BL antimonene/Bi(111) moiré superlattices in the momentum space. **a** 2D plot of ARPES intensity as a function of momentum k_x along the $\bar{\Gamma} - \bar{M}$ direction and as a binding energy E_B . **b** 2D plot of the SARPES signal as a function of momentum k_x along the $\bar{\Gamma} - \bar{M}$ direction and as a binding energy E_B . The intensity and the spin polarization in the y direction are indicated by brightness (dark: high, bright: low) and colour (red: positive, blue: negative), respectively. **c** 2D plot of ARPES intensity measured near the Fermi level ($E_B = 0.03$ eV) in the $k_x - k_y$ space, which gives the Fermi surface contour. The plot includes two data sets obtained in different runs, which causes an apparent discontinuity at $k_x = 0.12 \text{ \AA}^{-1}$. The dashed lines indicate the $\bar{\Gamma} - \bar{K}$ directions. The red ellipsoids show the locations of the saddle points of S_2 band.

E. DFT band structure calculations for the epitaxial Sb(111)/Bi(111) models

The DFT calculations were conducted for an epitaxial model of 1BL Sb(111) on 5BL Bi(111) (Fig. E1) and for an epitaxial model of 2BL Sb(111) on 5BL Bi(111) (Fig. E2). Here the results for the AA and AC stackings are displayed. Regarding the results for the AB stacking, see Fig. 4.

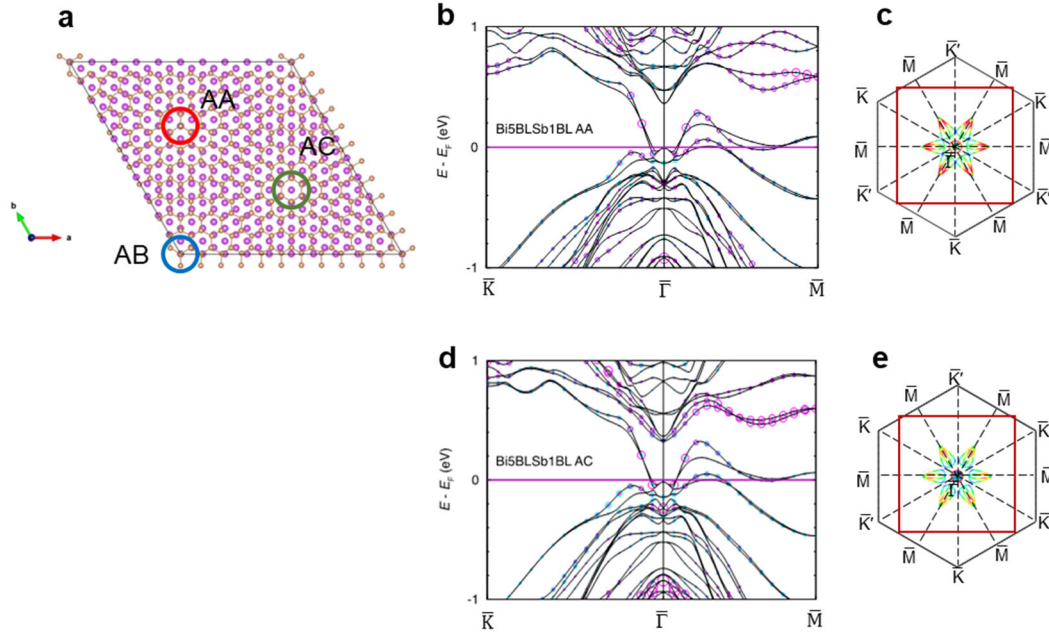


Fig. E1 | DFT band structure calculations for the 1BL Sb(111)/5BL Bi(111) epitaxial model.

a Atomic structures of the unit cell of the moiré superlattice for determining the locations of the Sb atoms in the out-of-plane direction. The red, blue and green circles shows the centres of the AA, AB and AC stacking regions, respectively. **b, d** Band dispersions along the $\bar{K} - \bar{\Gamma} - \bar{M}$ direction calculated for the AA stacking (**b**) and the AC stacking (**d**). **c, e** Fermi surfaces calculated for the AA stacking (**c**) and the AC stacking (**e**).

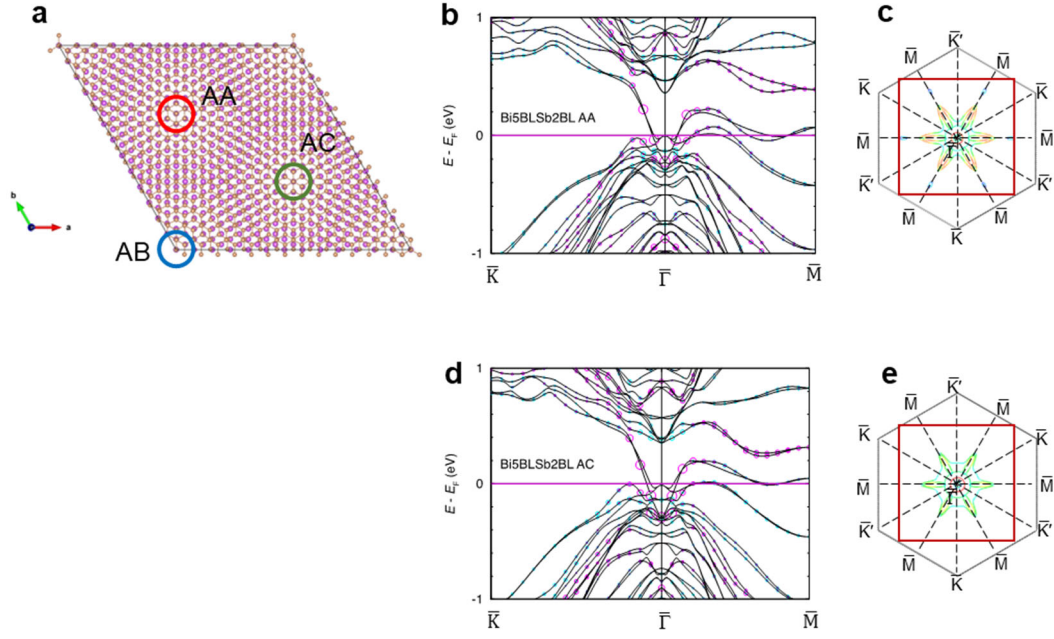


Fig. E2 | DFT band structure calculations for the 2BL Sb(111)/5BL Bi(111) epitaxial model.
a Atomic structures of the unit cell of the moiré superlattice for determining the locations of the Sb atoms in the out-of-plane direction. The red, blue and green circles shows the centres of the AA, AB and AC stacking regions, respectively. **b, d** Band dispersions along the $\bar{K} - \bar{\Gamma} - \bar{M}$ direction calculated for the AA stacking (**b**) and the AC stacking (**d**). **c, e** Fermi surfaces calculated for the AA stacking (**c**) and the AC stacking (**e**).