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Observation of van Hove Singularities in Twisted Silicene Multilayers

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Abstract
Interlayer interactions perturb the electronic structure of two-dimensional materials and lead to new physical phenomena, such as van Hove singularities and Hofstadter's butterfly pattern. Silicene, the recently discovered two-dimensional form of silicon, is quite unique, in that silicon atoms adopt competing sp2 and sp3 hybridization states leading to a low-buckled structure promising relatively strong interlayer interaction. In multilayer silicene, the stacking order provides an important yet rarely explored degree of freedom for tuning its electronic structures through manipulating interlayer coupling. Here, we report the emergence of van Hove singularities in the multilayer silicene created by an interlayer rotation. We demonstrate that even a large-angle rotation (>20°) between stacked silicene layers can generate a Moiré pattern and van Hove singularities due to the strong interlayer coupling in multilayer silicene. Our study suggests an intriguing method for expanding the tunability of the electronic structure for electronic applications in this two-dimensional material.

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Abstract: Interlayer interactions perturb the electronic structure of two-dimensional materials and lead to new physical phenomena, such as van Hove singularities and Hofstadter’s butterfly pattern. Silicene, the recently discovered two-dimensional form of silicon, is quite unique, in that silicon atoms adopt competing sp² and sp³ hybridization states leading to a low-buckled structure promising relatively strong interlayer interaction. In multilayer silicene, the stacking order provides an important yet rarely explored degree of freedom for tuning its electronic structures through manipulating interlayer coupling. Here, we report the emergence of van Hove singularities in the multilayer silicene created by an interlayer rotation. We demonstrate that even a large-angle rotation (>20°) between stacked silicene layers can generate a Moiré pattern and van Hove singularities due to the strong interlayer coupling in multilayer silicene. Our study suggests an intriguing method for expanding the tunability of the electronic structure for electronic applications in this two-dimensional material.

Low-energy electronic properties of few-layer two-dimensional (2D) materials are known to be strongly dependent on the stacking arrangement.1–3 Twisted bilayers in Dirac Fermion systems, e.g., graphene,4 are readily observed, which induce a crossover of Dirac cones that is attributed to rotation of the Brillouin zone (BZ). With interlayer coupling which ensures electron hopping between adjacent layers, the emergence of two saddle points in the band structure due to the overlaid Dirac cones gives rise to logarithmic van Hove singularities (vHs) in the density of states (DOS). When the vHs is close to the Fermi level (E_F), its magnified DOS results in electronic instability and consequently causes new phases of matter with desirable properties, for example, superconductivity, magnetism, and density waves.

Silicene5–12, a silicon-based Dirac Fermion material, has attracted extensive interest since its discovery due to its massless Dirac Fermion characteristics,7,10 strong spin–orbital coupling (SOC),13 and its great potential in electronic applications.8 The successful fabrication6,14–16 of silicene subverts the conventional wisdom on hybridization by proving that silicon atoms can form an sp³-sp³ hybridized state and crystallize into a 2D structure. Although recent scanning tunneling microscopy (STM) and Raman studies have demonstrated that the sp³ component is much relaxed by the low-buckled structure in silicene7,17 relatively strong interlayer coupling is still expected in multilayer silicene in contrast to the other 2D layered materials, such as graphene and boron nitride. How this strong interlayer interaction perturbs the electronic structure of multilayer silicene, and consequently, leads to new physical phenomena has been rarely studied to date.

In this work, we report that √3 × √3 multilayer silicene consists of the intrinsic 1 × 1 honeycomb structure with a strong interlayer coupling. The Moiré pattern and vHs were generated by an interlayer twisting in multilayer silicene with a rotation angle of 21.8°. Our results show that a Moiré superlattice gives rise to a periodic potential, which can modulate the electronic dispersion at vHs.

All silicene films investigated in this work were grown in a preparation chamber with base pressure ∼5 × 10⁻¹¹ Torr in a commercial low-temperature scanning tunneling microscopy system (LT-STM, Unisoku Co.). Clean Ag(111) substrates were prepared by argon ion sputtering followed by annealing to 820 K for several cycles. The silicene monolayers were then grown on the Ag(111) surfaces by evaporating silicon atoms from a heated silicon wafer with the substrate kept at 470 K.
The detailed growth method has been reported elsewhere.\textsuperscript{17–20} The differential conductance, $dI/dV$, spectra were acquired by using a standard lock-in technique with a 10 mV modulation at 613 Hz. All the measurements were carried out in an ultrahigh vacuum (UHV) at 77 K. Angle-resolved photoemission spectroscopy (ARPES) characterizations were performed at photoelectron spectroscopy station, Institute of High Energy Physics, Chinese Academy of Sciences. A monochromatized He–I light source (21.2 eV) was used for the band dispersion measurements.

Density functional theory (DFT) calculations were performed using the Vienna \textit{ab initio} simulation package (VASP) with the projector-augmented wave (PAW) method.\textsuperscript{21,22} The Perdew–Burke–Ernzerhof (PBE) correlation exchange functional at the GGA level was adopted. A Γ-centered (11 $\times$ 11 $\times$ 1) Monkhorst–Pack k-point grid was adopted in structural relaxation and energy calculations. All the calculations were carried out until the change in energy and the adopted in structural relaxation and energy calculations. All the density of states.\textsuperscript{21,22} The Perdew–Burke–Ernzerhof (PBE) correlation exchange functional at the GGA level was adopted. A Γ-centered (11 $\times$ 11 $\times$ 1) Monkhorst–Pack k-point grid was adopted in structural relaxation and energy calculations. All the calculations were carried out until the change in energy

Typical STM topographic image (50 nm $\times$ 50 nm, $V = -1$ V, $I = 3$ nA) of the multilayer silicone film. (b) STM image of $\sqrt{3} \times \sqrt{3}$ silicone structure (4 nm $\times$ 4 nm, $V = -3$ mV, $I = 4$ nA). Only the topmost atoms in the buckled silicone layer are observed, which are arranged in a honeycomb structure. The dashed black rhombus marks a $\sqrt{3} \times \sqrt{3}$ unit cell. (c) High-resolution STM image reveals that the $\sqrt{3} \times \sqrt{3}$ silicone is constructed from the 1 $\times$ 1 honeycomb structures (as indicated by the yellow honeycomb, 1 $\times$ 1 HC). The black dashed line represents the $\sqrt{3} \times \sqrt{3}$ unit cell ($\sqrt{3} \times \sqrt{3}$ UC). The ABÅ buckled structure is reflected by the brightness of the Si atoms. The yellow, blue, and red balls labeled in the $\sqrt{3} \times \sqrt{3}$ silicone unit cell denote the top, middle, and bottom silicon atoms, respectively (2 nm $\times$ 2 nm, $V = -3$ mV, $I = 4$ nA). (d) Height profile corresponding to the red dashed line in c. The inset is a side view of the ABÅ buckled structure corresponding to the height profile.

Supporting Information). In addition to the $\sqrt{3} \times \sqrt{3}$ structure, we also observed a pattern with a large period of about 1.7 nm on the top layer of the silicone film shown in Figure 2c, which has never been found in a single layer of silicone. Considering that the $\sqrt{3} \times \sqrt{3}$ lattice is still resolved in STM image (Figure 2e), we infer that this larger pattern is likely to be a Moiré pattern due to the lattice mismatch between the top layer and the underlying layer of silicone. If interlayer twisting induces the Moiré pattern, the relationship between the twisted lattices and the Moiré pattern can be described by the Moiré equations: $D = a/[2 \sin(\theta/2)]$,\textsuperscript{29} where $D$ is the periodicity of the Moiré pattern, $a$ is the lattice constant of $\sqrt{3} \times \sqrt{3}$ silicone, which is 0.64 nm, and $\theta$ is the interlayer rotation angle in twisted $\sqrt{3} \times \sqrt{3}$ silicone layers. Taking account of the Moiré periodicity of 1.7 nm, the value of angle $\theta$ is estimated to be around 21.8°. Furthermore, twisted angle $\theta$ could be related to the misorientation angle between the $\sqrt{3} \times \sqrt{3}$ silicone lattice and the Moiré superlattice $\phi$ as $\phi = 30° - \theta/2$. By using the value of $\theta = 21.8°$ obtained above, $\phi$ could be estimated to be around 19.1°, which is consistent with the experimental observation as shown in Figure 2d. Therefore, this angle confirms that the observed Moiré pattern on multilayer silicone originates from interlayer twisting. It is worth mentioning that 21.8° is the only observed twisting angle in our STM measurement, which may be the most energy favorable twisting angle in multilayer silicone. Interestingly, the protuberance and valley areas in the Moiré pattern can swap.
their positions under STM scanning, as demonstrated in Figure 2fg. The abrupt change in the protuberance and valley areas might result from the dynamic flip-flop motion (see Supporting Information), which is possibly induced by a structural buckling transition in $\sqrt{3} \times \sqrt{3}$ silicene.

Besides the Moiré pattern in the lattice structure, the twisting structure of multilayer silicene also leads to periodical variations of DOS in real space mapping. Figure 3 shows experimental and theoretically calculated DOS distribution at different energies for the Moiré pattern of twisted silicene multilayer. It is clear that at an energy lower than the Fermi level (Figure 3a,c,e), a hexagonal pattern of potential occurs. The centers of the hexagons show the highest density of states, while the edges show the lowest. However, the distribution of DOS is inverted at an energy higher than the Fermi level (e.g., Figure 3c,d,g,h). This is consistent with DOS variation of graphene on boron nitride (BN), which also shows invert contrast between positive and negative bias mapping. Near the Fermi level (Figure 3b,f), a combined feature of hexagonal and honeycomb lattices indicates a transition between these two types of DOS distribution, in contrast to random distributed electron and hole puddles of graphene on SiO$_2$, where many charged impurities are located at interface between graphene and SiO$_2$.

Exotic electronic properties can be induced by interlayer rotation in 2D layered materials, for instance, van Hove singularities (vHs) in twisted graphene layers$^1$ and a new set of Dirac Fermions in single layer graphene on BN.$^2$ Figure 4 shows scanning tunneling spectra (STS) collected on the Moiré pattern in the twisted silicene layers. As shown in Figure 4b, the bump at $-1.0 \text{ V}$ in STS is attributed to a flat band. The Dirac point at $-0.1 \text{ V}$ and flat band are observed in both Moiré and $\sqrt{3} \times \sqrt{3}$ silicene regions. Two prominent peaks at $-1.2$ and $0.75 \text{ V}$ can be seen in the STS spectrum taken from the Moiré regions, but are absent in the $\sqrt{3} \times \sqrt{3}$ silicene regions without interlayer twisting. The positions of these two peaks are slightly deviated from symmetry with respect to the Dirac point ($-0.1 \text{ V}$), which is most likely due to tip induced band...
bending.\(^{34,35}\) We attribute these peaks to interlayer-rotation-induced vHs in the DOS. The mechanism of interlayer-twisting-induced vHs is illustrated in Figure 4c,d. In twisted silicene layers, the Dirac cones corresponding to each layer are centered at different points in reciprocal space (indicated as K\(_1\) and K\(_2\)) due to rotation of the Brillouin zone (BZ) with the same twisting angle (\(\theta\)). Owing to interlayer electron hopping, the overlapping Dirac cones generate two saddle points that are symmetric with respect to the Dirac point. As a result, they give rise to two vHs peaks in the DOS. Figure 4c is a line profile consisting of 50 spectra collected along the dashed arrow in Figure 4a, which shows the spatial distribution of the vHs. It shows that the vHs peaks at 0.75 V and \(-1.2\) V in the twisted silicene can be effectively modulated by the periodic Moiré potential. The asymmetric peak intensity may result from the influence of the third layer of silicene, similar to the case of multilayer graphene.\(^1\)

In principle, it is well-known that the interlayer coupling parameter, \(t_{\theta}\), depends on the three-dimensional (3D) separation parameter \(R = (r^2 + d_\perp^2)^{1/2}\), where \(r\) is the spatial separation projected onto the plane, and \(d_\perp\) is the interlayer distance. The interlayer coupling is, therefore, modulated by the interlayer rotation, since \(R\) increases with increasing interlayer rotation angle (\(\theta\)). Experimentally, the interlayer coupling strength can be calculated\(^2\) by \(t_{\theta} = (\hbar v_F \Delta K - \Delta E_{\text{vHs}})/2\). Here, \(v_F\) is the Fermi velocity, \(\Delta K\) is the difference between the positions of the Dirac cones in reciprocal space, and \(\Delta E_{\text{vHs}}\) is the energy difference between the Dirac point and the vHs. Twisted graphene as an example, with small interlayer separation projected onto the plane, and \(d_\perp\) is about 0.108 eV,\(^{1,2}\) and consequently, the vHs is preserved. The interlayer coupling breaks down (\(t_{\theta} \approx 0\) eV) when \(\theta\) is greater than \(15^\circ\) in twisted graphene, and thus, the vHs vanishes.\(^{37,38}\) In the case of twisted silicene, the observed vHs corresponds to a large interlayer rotation angle \(\theta = 21.8^\circ\). It is worth noting that 21.8° is the largest rotation angle between two honeycomb lattices that can produce a commensurate superlattice.\(^1\) Considering that \(v_F\) is about \(5.0 \times 10^5\) ms\(^{-1}\) in twisted multilayer silicene from ARPES measurements (see Supporting Information), which also show vHs, \(t_{\theta}\) is calculated as 0.182 eV in the twisted multilayer silicene sample, which is even greater than it is in twisted graphene with \(\theta < 5^\circ\). Hence, it reflects the strong interlayer interaction in multilayer silicene. As observed in STM (Figure 1), the buckled AB\(_A\) mixed states indicates that silicon atoms take sp\(^2\)-sp\(^3\) mixed states in multilayer graphene. The partial sp\(^3\) components enhance electron hopping between adjacent layers, in comparison to the case of pure sp\(^2\) states, which leads to a stronger interlayer interaction in silicon in contrast to graphene. The energy difference between vHs is 1.95 eV, which indicates that the optical absorption of visible light would be achieved in twisted silicene multilayers. It paves a way to develop ultrathin optical devices by using this 2D Dirac-Fermion material.

In conclusion, we have observed the Moiré pattern and vHs in twisted multilayer silicene. The existence of the \(1 \times 1\) low-buckled AB\(_A\) structure has been confirmed. The silicon sp\(^2\)-sp\(^3\) mixed hybridization states lead to a robust interlayer interaction in multilayer silicene, which is much stronger than the interlayer interaction in graphene. It ensures electron hopping between the twisted silicene layers, even with a large interlayer rotation angle. The experimental observations suggest a possible way to engineer electronic properties in multilayer silicene by interlayer twisting.


