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.

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 electron hopping between adjacent layers, 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 evaporation of silicon atoms from a heated silicon wafer with the substrate kept at 470 K.

Received: May 24, 2016
Published: July 26, 2016
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 the 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 by 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 × 11 × 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 force on each atom were less than 1 × 10\textsuperscript{−6} eV per cell and 1 × 10\textsuperscript{−5} eV/Å, respectively.

To investigate the electronic properties of multilayer silicene, we prepared a sample of multilayer silicene (thickness >5 unit cells) on a Ag(111) surface by molecular beam epitaxial (MBE). Figure 1a presents an STM image indicating the morphology of the multilayer silicene on the Ag(111) surface. A well-defined $\sqrt{3} \times \sqrt{3}$ honeycomb structure is demonstrated in the top layer of silicene, as shown in Figure 1b. Nevertheless, the $\sqrt{3} \times \sqrt{3}$ honeycomb lattice only consists of the upper buckled silicon atoms, and the detailed structure of the lower silicon atoms is missing. The higher resolution STM images are required to resolve all silicon atoms in silicene lattice. The formation of the “supershape” tip composed by p-wave molecule is used as the critical technique for the resolution enhancement of STM images, because spatial derivatives of the sample wave functions will be resolved by the p-wave tip state.\textsuperscript{23,24} Recently, by applying this technique on the p-wave atom Si, subatomic resolution of Si(111)-(7 × 7) surface is achieved by a Si-terminated tip.\textsuperscript{25} In our experiment, in order to obtain the Si-terminated tip, we use an extremely small tip−sample distance to introduce a controllable contact between tip and silicene surface during scanning. A new buckled honeycomb arrangement with smaller lattice parameter ($a \approx 0.38$ nm), which is close to the periodicity of $1 \times 1$ silicene, is explored and shown in Figure 1c after the formation of Si-terminated tip. Furthermore, the Si atoms in one $\sqrt{3} \times \sqrt{3}$ unit cell have three different apparent heights, as shown in Figure 1d, which is identical to the predicted ABA model for $1 \times 1$ silicene in previous work. Thus, Figure 1c displays the integrated atomic arrangement of $1 \times 1$ silicene, where the lower-buckled silicon atoms were also resolved. It should be noted that $\sqrt{3} \times \sqrt{3}$ Ag on Si(111) substrate is isostructural to the $\sqrt{3} \times \sqrt{3}$ silicene superstructure, leading to the debate on the presence or absence of $\sqrt{3} \times \sqrt{3}$ silicene phase.\textsuperscript{26} Resolved lower-buckled silicon atoms in silicene provide a solid evidence to clarify this debate. The honeycomb-chained triangle (HCT) model and inequivalent triangle (IET) model\textsuperscript{27,28} were used to describe the atomic structure of the Si(111)-$\sqrt{3} \times \sqrt{3}$ Ag surface, where each protrusion in STM images is contributed by one Ag trimer. However, these Ag trimers do not exist on $\sqrt{3} \times \sqrt{3}$ silicene from atomic resolution STM image (Figure 1c), excluding the possibility of Ag-terminated Si(111) reconstruction. More results of the distinct features between $\sqrt{3} \times \sqrt{3}$ silicene and $\sqrt{3} \times \sqrt{3}$ Ag reconstruction are identified by STS, \textit{in situ} Raman spectra and surface reactivity investigation (see 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 silicene film shown in Figure 2c, which has never been found in a single layer of silicene. 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 silicene. 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 $\sqrt{3} \times \sqrt{3}$ silicene, which is 0.64 nm, and $\theta$ is the interlayer rotation angle in twisted $\sqrt{3} \times \sqrt{3}$ silicene 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 $\sqrt{3} \times \sqrt{3}$ silicene 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 silicene 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 silicene. Interestingly, the protuberance and valley areas in the Moiré pattern can swap

![Figure 1. $\sqrt{3} \times \sqrt{3}$ silicene film and $1 \times 1$ honeycomb structure. (a) Typical STM topographic image (50 nm × 50 nm, $V = -1$ V, $I = 5$ nA) of the multilayer silicene film. (b) STM image of $\sqrt{3} \times \sqrt{3}$ silicene structure (4 nm × 4 nm, $V = -3$ mV, $I = 4$ nA). Only the topmost atoms in the buckled silicene 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 $\sqrt{3} \times \sqrt{3}$ silicene 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 ABA buckled structure is reflected by the brightness of the Si atoms. The yellow, blue, and red balls labeled in the $\sqrt{3} \times \sqrt{3}$ silicene unit cell denote the top, middle, and bottom silicon atoms, respectively (2 nm × 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 ABA buckled structure corresponding to the height profile.](image-url)
Figure 2. Moiré pattern in twisted $\sqrt{3} \times \sqrt{3}$ multilayer silicene. (a) Morphology of multilayer silicene (30 nm × 30 nm, $V = -1.5$ V, $I = 100$ pA). Regions 1 and 2 indicate a Moiré region and a $\sqrt{3} \times \sqrt{3}$ region, respectively. (b) Schematic diagram of Moiré pattern induced by interlayer twisting in multilayer silicene with a rotation angle ($\theta$) of 21.8°. (c) Enlarged STM image of Region 1 in (a) shows a Moiré superlattice with a lattice constant of 1.7 nm. The Moiré unit cell is outlined by the black rhombus (6 nm × 6 nm, $V = -0.5$ V, $I = 100$ pA). (d) STM image indicates a misorientation angle ($\phi$) of 19.1° between the $\sqrt{3} \times \sqrt{3}$ and the Moiré lattices. (e) Enlarged STM image of Region 2 in (a) demonstrates a $\sqrt{3} \times \sqrt{3}$ structure in adjacent layers without interlayer rotation. The unit cell of $\sqrt{3} \times \sqrt{3}$ silicene is outlined in green. (f) and (g) Flip-flop behavior of the Moiré pattern in a continuous STM scan, which demonstrates the swapping of protuberances and valleys in the Moiré superlattice, as marked by the arrows (20 nm × 20 nm, $V = -0.5$ V, $I = 100$ pA).

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,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 a 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 and a new set of Dirac Fermions in single layer graphene on BN.

Figure 3. Experimental STS mappings and theoretical images of DOS for moiré pattern of twisted silicene multilayer at different energies. (a, e) −0.5 V, (b, f) −0.1 V, (c, g) 0.4 V, (d, h) 0.5 V. The size of all images is 6 nm. (a–d) Experimental STS mappings for moiré pattern at different bias voltages. STS mapping below and above Fermi surface shows hexagonal and honeycomb lattice, respectively. (e–h) Corresponding theoretical calculated DOS distributions. The scales bars in all images are 2 nm.

Figure 4. Van Hove singularities in DOS originate from interlayer twisting in multilayer silicene. (a) STM image of Moiré pattern ($V = 1$ V, $I = 100$ pA). (b) STS carried out in the Moiré region (Figure 2c; set point: $V = 1$ V, $I = 100$ pA) and in the $\sqrt{3} \times \sqrt{3}$ silicene region (Figure 2e; set point: $V = 1$ V, $I = 100$ pA). (c) and (d) Illustrations of vHs that originates from twisted silicene layers. The interlayer twisting with the angle $\theta$ leads to a rotation of the BZ with the same angle. The Dirac cones corresponding to $K_1$ and $K_2$ are offset to each other by $\Delta K$. The shifted Dirac cones create saddle points that induce two vHs peaks in the DOS. (e) 50 spectra collected along the black arrow in (a) (from bottom to top; set point: $V = 1$ V, $I = 100$ pA).
bending.\textsuperscript{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 4e 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.\textsuperscript{1}

In principle, it is well-known that the interlayer coupling parameter, $t_{\theta}$, depends on the three-dimensional (3D) separation parameter\textsuperscript{26} $R = (r^2 + d_z^2)^{1/2}$, where $r$ is the spatial separation projected onto the plane, and $d_z$ 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\textsuperscript{2} by $t_{\theta} = (\hbar v_F \Delta K - \Delta E_{\text{vHs}})/\sqrt{2}$. 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. When twisted graphene as an example, with small interlayer rotation angles ($<5^\circ$), $t_{\theta}$ is about 0.108 eV,\textsuperscript{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.\textsuperscript{17,30} 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 $21.8^\circ$ is the largest rotation angle between two honeycomb lattices that can produce a commensurate superlattice.\textsuperscript{1} Considering that $v_F$ is about $5.0 \times 10^5$ m s$^{-1}$ 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\text{Ä} structure indicates that silicon atoms take sp$^3$–sp$^3$ mixed states in multilayer silicene. 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 silicene 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\text{Ä} structure has been confirmed. The silicon sp$^3$–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.

## ACKNOWLEDGMENTS

This work was supported by the Australian Research Council (ARC) through a Discovery Project (DP 140102581 and DP160102627), the Ministry of Science and Technology (MOST) of China (Grant No. 2013CB901601), and the National Natural Science Foundation (NSF) of China (Grant Nos. 11334011, 11322431, 11575227, and 61474097). The authors also acknowledge the financial supported by the University of Wollongong through a University Research Council (URC) Small Grant. Z.L. would like to acknowledge support by the University of Wollongong through the Vice Chancellor’s Postdoctoral Research Fellowship Scheme. We gratefully acknowledge discussions with Zheng Liu, Chao Zhang, Zhongshuai Ma, and Feng Liu. The authors thank Dr. T. Silver for valuable support and assistance.

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