Evidence of Dirac fermions in multilayer silicene

Paola De Padova,[1,a)] Patrick Vogt,[2,3] Andrea Resta,[3] Jose Avila,[4] Ivy Razado-Colambo,[3,4] Claudio Quaresima,[1] Carlo Ottaviani,[1] Bruno Olivieri,[5] Thomas Bruhn,[3,2] Toru Hirahara,[6] Terufusa Shirai,[6] Shuji Hasegawa,[6] Maria Carmen Asensio,[4] and Guy Le Lay[3,1]
[1]*Consiglio Nazionale delle Ricerche-ISM, via Fosso del Cavaliere, 00133 Roma, Italy*
[2]*Technische Universität Berlin, Institut für Festkörperphysik, Hardenbergstrasse 36, 10623 Berlin, Germany*
[3]*Aix-Marseille University, CINaM-CNRS, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France*
[4]*Synchrotron SOLEIL, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France*
[5]*Consiglio Nazionale delle Ricerche-ISAC, via Fosso del Cavaliere, 00133 Roma, Italy*
[6]*Department of Physics, School of Science, University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

(Received 20 February 2013; accepted 4 April 2013; published online 23 April 2013)

Multilayer silicene, the silicon analogue of multilayer graphene, grown on silver (111) surfaces, possesses a honeycomb ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction, observed by scanning tunnelling microscopy at room temperature, past the initial formation of the dominant, 3×3 reconstructed, silicene monolayer. For a few layers silicene film we measure by synchrotron radiation photoelectron spectroscopy, a cone-like dispersion at the Brillouin zone centre due to band folding. π^* and π states meet at ∼0.25 eV below the Fermi level, providing clear evidence of the presence of gapless Dirac fermions. © *2013 AIP Publishing LLC* [http://dx.doi.org/10.1063/1.4802782]

Silicene, graphene's cousin,[1] is a single layer of silicon atoms arranged in a two-dimensional (2D) honeycomb lattice. Its occurrence was first theorized some years ago,[2–6] but only recently it has been synthesized as a silicon allotrope, which does not exist in nature.[7–17] This new form of silicon has recently attracted considerable interest, because its topology confers to it the same remarkable electronic properties as those of graphene, with the potential advantage of being easily integrated in current Si-based nano/micro-electronics devices.[18] Silicene has been shown to exhibit massless relativistic behavior for its quasiparticles in the vicinity of the Dirac points[7,13] with a very high Fermi velocity, similar to that of free standing graphene.[19]

Single layer epitaxial silicene grown on silver (111) surfaces forms a 4×4 super cell with respect to the substrate as shown in Scanning Tunnelling Microscopy (STM) and low energy electron diffraction (LEED) experiments;[7,8] in other words, in real space, the 3 lattice vectors of silicene exactly match the 4 lattice vectors of silver. Consequently, the aforementioned 4×4 supercell corresponds to a 3×3 reconstruction of silicene. (We shall refer to this correspondence throughout the present letter by the notation 3×3.) Synchrotron radiation angle-resolved photoelectron spectroscopy measurements have shown that the silicene π band produces a linear dispersion attributed to a Dirac cone.[7]

A ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction with respect to silicene has recently been reported and interpreted as arising from both second layer silicene atoms, as well as from those in direct contact with the silver substrate.[13] The occurrence of bilayer or multilayer graphenes are well-documented,[16,20–25] typically forming on silicon carbide. A similar behaviour might well be expected for silicene,[26–28] which could also potentially arise the multilayer stacking. Band structure theoretical calculations under electrical field[29] for both free-standing and bilayer silicene, in a Bernal-type stacking, predict electronic properties akin to those of topological insulators. In this bilayer silicene, the gap closes due to the trigonal warping effect.[29]

In this letter, we give a direct evidence of the key electronic signature of Dirac fermions in multilayer silicene grown on Ag(111) substrates at room temperature (RT), as recently obtained by Vogt *et al.*[30] The growth of silicene on Ag(111) determined by Auger electron spectroscopy (AES) corresponds to a layer-plus-island mode, where epitaxial silicene islands, oberved by STM display a $\sqrt{3} \times \sqrt{3}$-R(30°) reconstruction with respect to free standing silicene. These islands grow past one monolayer silicene sheet, which has dominantly 3×3 and occasionally $\sqrt{7} \times \sqrt{7}$-R(±19°1) coincidence cells.[8] We have observed the presence of $\sqrt{3} \times \sqrt{3}$-R(30°) reconstruction up to level 13 of these multilayer silicene islands.[30] Angle-resolved photoemission spectroscopy measurements (ARPES) has especially revealed the existence of Dirac fermions at the center ($\overline{\Gamma}_0$ point) of the Brillouin zone (BZ), where the K and K′ points of 1×1 silicene BZ fold due to the $\sqrt{3} \times \sqrt{3}$-R(30°) reconstruction.

The Ag(111) substrate was cleaned in the UHV chamber (base pressure: 7.0×10^{-11} mbar) by repeatedly sputtering with Ar^+ ions and annealing the substrate at 750 K, while keeping the pressure below 1×10^{-10} mbar during heating. An infrared pyrometer and a thermocouple were used to measure the sample temperature. Si was evaporated at a rate of ∼0.03 ML/min from a Si source. AES/LEED measurements/observations have been performed at CNR-ISM (Roma, Italy), whereas STM/LEED observations have been performed at the CNRS-CINaM (Marseille, France). The Ag substrate was kept at T ∼ 470 K to produce the (3×3) single layer epitaxial silicene (giving a (4×4) LEED pattern with reference to Ag(111)) and next multilayer islands. The silicene growth curve was obtained by Auger electron spectroscopy at 470 K and LEED patterns were recorded at each

[a)]Author to whom correspondence should be addressed. Electronic mail: paola.depadova@ism.cnr.it. Tel.: +39-06-49934144. Fax: +39-06-49934153.

measured point at RT. The STM images were recorded at RT in constant-current mode. The z-piezo drive has been precisely calibrated with the 0.24 nm height of a monoatomic Ag(111) step of the bare surface. AES and/or X-ray photoemission spectroscopy measurements made after each silicene deposition never showed surface contaminants. ARPES data for Si covered Ag(111) surfaces characterized by their LEED patterns have been taken at the ANTARES beamline of the French (SOLEIL, Saint Aubin) synchrotron radiation facilities with energy resolution better than 20 meV. The photoemission spectra were acquired at RT by using the angular resolved mode of the electron energy analyser with an acceptance of ~24° and ~30° (SCIENTA R4000). The photon energy was set to 126 eV. All the energies are referred to the Fermi level $E_{F.}$

We have investigated the growth mode of silicon on silver (111) at ~470 K by recording both silicon LVV and silver MNN AES signals while correlatively observing the evolution of the LEED patterns (Fig. 1(a)). The variation of the AES signals directly reveals a layer-plus-islands growth mode.[31] At each step of Si coverage, a LEED pattern was acquired at RT. Below one monolayer coverage (1 ML) the 3×3 silicene structure was observed where all one-third order spots were observed, in good agreement with the literature.[7,8] At this growth temperature, we have obtained an almost pure 3×3 silicene phase; still, a weak $\sqrt{7} \times \sqrt{7}$-R(±19°1) contribution can be noticed as two extra spots on each side of the integer order silicene spots.[32] After completion of one monolayer, the 1/3,1/3 order silicene spots (and their symmetric equivalents) become markedly stronger in intensity, subsequently yielding a pure $\sqrt{3} \times \sqrt{3}$-R(30°) LEED pattern (From here on $\sqrt{3} \times \sqrt{3}$). This last symmetry persists up to rather high silicon coverages (~10 MLs equivalent).

In accord with the observations of Arafune *et al.*,[32] the second layer islands display a $\sqrt{3} \times \sqrt{3}$ unit cell in STM imaging (with reference to silicene) (see Fig. 1(b)). We note that the $\sqrt{3} \times \sqrt{3}$ structure has been previously observed by STM at low temperature by Feng *et al.*[12] as the one silicene monolayer. At variance, at RT, Fig. 1(c), unambiguously assigns it to the second silicene layer: we have never observed direct growth (layer in contact with silver) of the $\sqrt{3} \times \sqrt{3}$ structure at RT.

During synchrotron radiation photoemission measurements we confirmed the layer-plus-islands silicene growth mode upon recording the Si 2*p*/Ag 3*d* core-level intensity ratios versus Si coverage at ~470 K. Then, ARPES was used to obtain the key electronic signature of multilayer $\sqrt{3} \times \sqrt{3}$ silicene. In reciprocal space, the arrangement of BZs of such epitaxial silicene layers is depicted in Fig. 2(a); it pinpoints the electronic properties of epitaxial silicene. Indeed, directly associated to the coincidence cell, the expected band folding could give rise to a Dirac cone at the zone centre $\overline{\Gamma}_0$ because the $\overline{K}_{(1\times1)\text{Silicene}}$ and $\overline{K}'_{(1\times1)\text{Silicene}}$ points fold right there.

Indeed, we found Λ- and V-shape bands at $\overline{\Gamma}_0$ as shown in Fig. 2(b), where the dispersion is collected at $\overline{\Gamma}_0$ (along $\overline{\Gamma} \rightarrow \overline{K}_{\text{silicene}}$) on $(\sqrt{3} \times \sqrt{3})$ silicene (4.5 equivalent silicene MLs). The waterfall line profiles of the dispersion are displayed in Fig. 2(c) as a guide for the eyes. These features are more and more evident as a function of silicene multilayer stacking formation.

We assign the Λ- and V-shape linear bands to π and π* Dirac cones stemming from $(\sqrt{3} \times \sqrt{3})$ multilayer silicene. The π* states are partially filled, due to charge transfer from the Ag(111) substrate, while no gap between the π and π* bands is detected; their crossing locates the Dirac point at ~0.25 eV. Furthermore, a very high RT Fermi velocity of $\sim 0.3 \times 10^6\,\text{ms}^{-1}$ is obtained, still a bit smaller than that obtained by empty states STM measurements of quantum interference patterns at low temperature by Chen *et al.*[13] We note another structure inside the π cone, which we assign to the remaining 3×3 silicene layer, due to the layer-plus-islands growth mode described above.

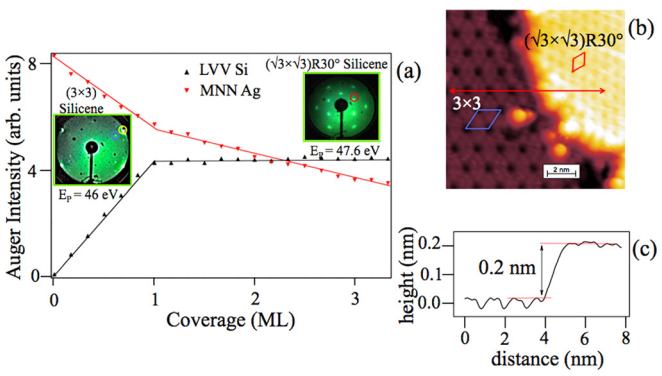

FIG. 1. Layer-plus-islands growth mode of silicon on Ag(111). (a) Auger signals versus coverage measured at ~470 K and corresponding LEED patterns: 3×3 initial silicene pattern followed after the break by the development of $\sqrt{3} \times \sqrt{3}$ silicene patterns, as taken at about 3.5 MLs (yellow, blue, and red circles represent, respectively, e.g., the (1,0) Ag spot and the (1,0) as well as (1/3,1/3) silicene spots). (b) STM topograph obtained at RT of one monolayer 3×3 silicene and of a $\sqrt{3} \times \sqrt{3}$ second layer island (filled states STM image: $9 \times 9\ \text{nm}^2$, $U_{bias} = -1.1$ V, I = 0.33 nA); the 3×3 and $\sqrt{3} \times \sqrt{3}$ cells are indicated. (c) Profile along the red line indicated in (b); the height of the second layer $\sqrt{3} \times \sqrt{3}$ structure is 0.2 nm above the 3×3 layer, differing significantly from a silver step height (0.24 nm).

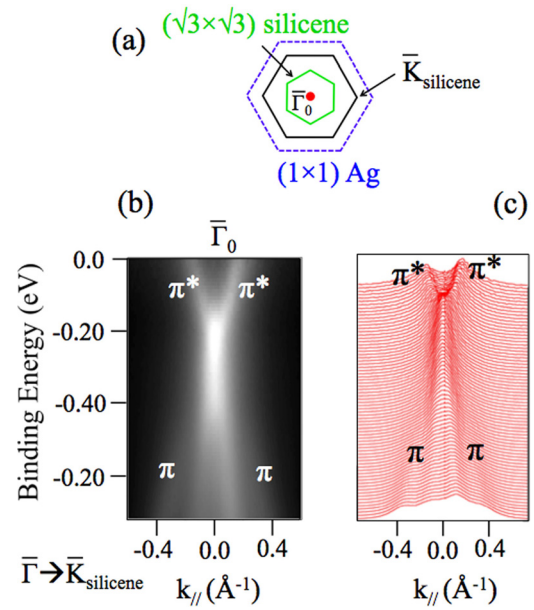

FIG. 2. Dirac fermionics of multilayer $(\sqrt{3} \times \sqrt{3})$R30° silicene islands: (a) Scheme of Brillouin zones; (b) Λ- and V-shape linear π and π* silicene bands ($h\nu = 126$ eV) at $\overline{\Gamma}_0$ (along $\overline{\Gamma} \rightarrow \overline{K}_{\text{silicene}}$) and (c) Waterfall line profiles of the dispersion displayed in (b) as a guide for the eyes.

When we compare with our previous results on the 3×3 silicene layer, where the Dirac point was estimated at ~ 0.3 eV (in fair agreement with the present value) and no π^* band was detected,[7] the closure of the gap is in perfect accord with the prediction of Ezawa for bilayer silicene.[29] On the contrary we note that our findings contradict the theoretical calculations on $(\sqrt{3} \times \sqrt{3})$R30° silicene by Chen *et al.*, where the π^* bands were found completely empty.[14]

The multilayer situation probably modifies the charge transfer to the upper silicene layer, as in graphene grown on different surfaces, where the substrate interaction can open a gap and the charge transfer can pull down the π^* branch.[33–35] The situation is comparable with that of graphene epitaxially grown on SiC substrates where a 0.26 eV gap is found. This gap narrows as the number of graphene layers increases, approaching zero when this number exceeds four.[36]

We stress that similar results have been recently obtained on multilayer silicene nano ribbons grown on Ag(110) surfaces, where the upward and downward shifts of the π and π^* bands result in the narrowing of the gap due to the increasing separation from the Ag(110) substrate of the silicene layers, stacked as they are in graphite.[37]

In summary, our ARPES results have given a clear signature of the presence of Dirac fermions in multilayer silicene with $(\sqrt{3} \times \sqrt{3})$R30° reconstruction.

Due to its intrinsic spin-orbit coupling and buckled honeycomb geometry, epitaxial silicene can be considered akin to a two-dimensional topological insulator, as recently predicted by Ezawa,[29] characterized by a gap in the single monolayer, but exhibiting no gap in the multilayer system.

Multilayer silicene offers interesting potentialities to this silicon allotrope; being *per se* directly compatible with silicon micro and nano technologies, which may very well lead to opening routes for innovative device conception and fabrication.

This work was supported by the "*2D-NANOLATTICES*" project of the Future and Emerging Technologies (FET) program within the 7th framework program for research of the European Commission, under FET Grant No. 270749, the Project for International Scientific Cooperation (PICS) Italy/France under Grant No. 40237, and the Deutsche Forschungsgemeinschaft (DFG) under Grant No. VO1261/3-1. The authors thank A. Ranguis for precious help in the STM measurements and the expert staffs of SOLEIL and ANTARES.

[1]"Graphene's silicon cousin" (editorial), Nature **485**, 9 (2012).
[2]G. G. Guzmán-Verri and L. C. Lew Yan Voon, Phys. Rev. B **76**, 075131 (2007).
[3]S. Lebègue and O. Eriksson, Phys. Rev. B **79**, 115409 (2009).
[4]S. Cahangirov, M. Topsakal, E. Aktuerk, H. Sahin, and S. Ciraci, Phys. Rev. Lett. **102**, 236804 (2009).
[5]D. Kaltsas, L. Tsetseris, and A. Dimoulas, J. Phys.: Condens. Matter **24**, 442001 (2012).
[6]E. Scalise, M. Houssa, G. Pourtois, B. van den Broek, V. Afanas'ev, and A. Stesmans, Nano Res. **6**, 19 (2013).
[7]P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. Le Lay, Phys. Rev. Lett. **108**, 155501 (2012).
[8]C.-L. Lin, R. Arafune, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi, and M. Kawai, Appl. Phys. Express **5**, 045802 (2012).
[9]A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang, and Y. Yamada-Takamura, Phys. Rev. Lett. **108**, 245501 (2012).
[10]D. Chiappe, C. Grazianetti, G. Tallarida, M. Fanciulli, and A. Molle, Adv. Mater. **24**, 5088 (2012).
[11]G. Le Lay, P. De Padova, A. Resta, T. Bruhn, and P. Vogt, J. Phys. D: Appl. Phys. **45**, 392001 (2012).
[12]B. Feng, Z. Ding, S. Meng, Y. Yao, X. He, P. Chen, L. Chen, and K. Wu, Nano Lett. **12**, 3507 (2012).
[13]L. Chen, C.-C. Liu, B. Feng, X. He, P. Cheng, Z. Ding, S. Meng, Y. Yao, and K. Wu, Phys. Rev. Lett. **109**, 56804 (2012).
[14]L. Chen, H. Li, B. Feng, Z. Ding, J. Qiu, P. Cheng, K. Wu, and S. Meng, Phys. Rev. Lett. **110**, 085504 (2013).
[15]J. Gao and J. Zhao, Sci. Rep. **2**, 1 (2012).
[16]M. Xu, T. Liang, M. Shi, and H. Chen, "Graphene-Like Two-Dimensional Materials," Chem. Rev. (published online), and references therein.
[17]C.-L. Lin, R. Arafune, K. Kawahara, M. Kanno, N. Tsukahara, E. Minamitani, Y. Kim, M. Kawai, and N. Takagi, Phys. Rev. Lett. **110**, 076801 (2013).
[18]Z. Ni, Q. Liu, K. Tang, J. Zheng, J. Zhou, R. Qin, Z. Gao, D. Yu, and J. Lu, Nano Lett. **12**, 113 (2012).
[19]K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature **438**, 197 (2005).
[20]T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenberg, Science **313**, 951 (2006).
[21]T. Ohta, A. Bostwick, J. L. McChesney, T. Seyller, K. Horn, and E. Rotenberg, Phys. Rev. Lett. **98**, 206802 (2007).
[22]K. V. Emtsev, F. Speck, Th. Seyller, and L. Ley, Phys. Rev. B **77**, 155303 (2008).
[23]M. Sprinkle, D. Siegel, Y. Hu, J. Hicks, A. Tejeda, A. Taleb-Ibrahimi, P. Le Fèvre, F. Bertran, S. Vizzini, H. Enriquez, S. Chiang, P. Soukiassian, C. Berger, W. A. de Heer, A. Lanzara, and E. H. Conrad, Phys. Rev. Lett. **103**, 226803 (2009).
[24]E. Moreau, S. Godey, F. J. Ferrer, D. Vignaud, X. Wallart, J. Avila, M. C. Asensio, F. Bournel, and J.-J. Gallet, Appl. Phys. Lett. **97**, 241907 (2010).
[25]A. S. Mayorov, D. C. Elias, M. Mucha-Kruczynski, R. V. Gorbachev, T. Tudorovskiy, A. Zhukov, S. V. Morozov, M. I. Katsnelson, V. I. Fal'ko, A. K. Geim, and K. S. Novoselov, Science **333**, 860 (2011).
[26]K. Takeda and K. Shiraishi, Phys. Rev. B **50**, 14916 (1994).
[27]Y. C. Wang, K. Scheerschmidt, and U. Gösele, Phys. Rev. B **61**, 12864 (2000).
[28]C. Kamal, A. Chakrabarti, A. Banerjee, and S. K. Deb, J. Phys.: Condens. Matter **25**, 085508 (2013).
[29]M. Ezawa, Eur. Phys. J. B **85**, 363 (2012); J. Phys. Soc. Jpn. **81**, 104713 (2012).
[30]P. Vogt, A. Resta, T. Bruhn, P. De Padova, and G. Le Lay, "Synthesis of graphitic silicon by multi-layer stacking of silicene," Scientific Reports (submitted).
[31]Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).
[32]R. Arafune, C.-L. Lin, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi, and M. Kawai, Surf. Sci. **608**, 297 (2013).
[33]K. Novoselov, Nature Mater. **6**, 720 (2007).
[34]A. Grüneis, K. Kummer, and D. V. Vyalikh, New J. Phys. **11**, 073050 (2009).
[35]I. Pletikosić, M. Kralj, P. Pervan, R. Brako, J. Coraux, A. T. N'Diaye, C. Busse, and T. Michely, Phys. Rev. Lett. **102**, 056808 (2009).
[36]S. Y. Zhou, G.-H. Gweon, J. Graf, A. V. Fedorov, P. N. First, W. A. De Heer, D.-H. Lee, F. Guinea, A. H. Castro Neto, and A. Lanzara, Nature Mater. **6**, 770 (2007).
[37]P. De Padova, O. Kubo, B. Olivieri, C. Quaresima, T. Nakayama, M. Aono, and G. Le Lay, Nano Lett. **12**, 5500 (2012); P. De Padova, C. Quaresima, C. Ottaviani, P. M. Sheverdyaeva, P. Moras, C. Carbone, D. Topwal, B. Olivieri, A. Kara, H. Oughaddou, B. Aufray, and G. Le Lay, Appl. Phys. Lett. **96**, 261905 (2010).