

## Ordered and Reversible Hydrogenation of Silicene

Jinglan Qiu,<sup>1</sup> Huixia Fu,<sup>1</sup> Yang Xu,<sup>1,2</sup> A. I. Oreshkin,<sup>1,3</sup> Tingna Shao,<sup>1</sup> Hui Li,<sup>1</sup> Sheng Meng,<sup>1</sup> Lan Chen,<sup>1,\*</sup> and Kehui Wu<sup>1,4,†</sup>

<sup>1</sup>*Institute of Physics, Chinese Academy of Science, Beijing 100190, China*

<sup>2</sup>*Department of Physics, Yunnan University, Kunming 650091, China*

<sup>3</sup>*Moscow State University, Department of Physics, Moscow 119992, Russian Federation*

<sup>4</sup>*Collaborative Innovation Center of Quantum Matter, Beijing 100871, China*

(Received 9 October 2014; revised manuscript received 18 January 2015; published 23 March 2015)

The hydrogenation of monatomic silicene sheet on Ag(111) was studied by scanning tunneling microscopy and density functional theory calculations. It was observed that hydrogenation of silicene at room temperature results in a perfectly ordered  $\gamma$ -( $3 \times 3$ ) superstructure. A theoretical model, which involves seven H atoms and rearranged buckling of Si atoms, was proposed and agrees with experiments very well. Moreover, by annealing to a moderate temperature, about 450 K, a dehydrogenation process occurs and the clean silicene surface can be fully recovered. Such uniformly ordered and reversible hydrogenation may be useful for tuning the properties of silicene as well as for controllable hydrogen storage.

DOI: 10.1103/PhysRevLett.114.126101

PACS numbers: 68.37.Ef, 61.48.-c, 68.43.Bc, 68.43.Fg

Graphene and silicene [1–3] are two elemental 2D materials discovered so far, consisting of a single sheet of C and Si atoms, respectively. Both graphene and silicene host a Dirac fermion state that induces exotic spintronic and optoelectronic properties [4–9]. To explore these effects, in many cases it requires a control of the electronic state, for example, doping or opening a gap at the Dirac point. Hydrogenation was found as an effective chemical method to modify the electronic property of graphene, where a dramatic band-gap opening was observed upon graphene hydrogenation [10–12]. However, in the case of graphene, the stable aromatic  $\pi$ -bond network makes it difficult either to attach or detach hydrogen atoms on carbon atoms. Indeed, it has been generally observed that hydrogen atoms on graphene form clusters instead of an ordered structure, and that a rather high temperature was needed to desorb hydrogen atoms [13]. In contrast to graphene, silicene possesses hybrid  $sp^2$ - $sp^3$  bonding which should naturally favor low-barrier hydrogen attach-detach processes. Hydrogenation could also be a promising method to modify the properties of silicene. Theoretical calculations suggested intriguing properties in hydrogenated silicene, for example, large gap ( $\sim 3$  eV) opening [14], and interesting ferromagnetic [15] and optoelectronic properties [16]. Various hydrogen-adsorption configurations (for example, both-sides adsorption and one-side adsorption that correspond to freestanding and substrate-supported silicene) have been studied theoretically [14,15,17]. However, so far there is still no experimental report on silicene hydrogenation.

In this Letter, we report on a study on the hydrogenation of monolayer silicene on an Ag(111) surface by scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. In contrast to the graphene

case, where hydrogen tends to form clusters, hydrogenated silicene exhibits a perfectly long-range ordered structure, namely, the  $\gamma$ -( $3 \times 3$ ) structure. Combining with first-principles calculations, we have determined that there are seven hydrogen atoms in each ( $3 \times 3$ ) unit cell and that the buckling configuration of Si atoms in silicene spontaneously rearranges upon hydrogenation. Moreover, by annealing the sample to a moderate temperature, about 450 K, dehydrogenation occurs and a clean silicene surface is recovered. Our work provides a clear and fundamental picture for silicene hydrogenation. And such a uniformly ordered, reversible hydrogenation can be useful to control the electronic properties of silicene for potential applications.

Experiments were carried out in a home-built low-temperature STM with a base pressure of  $1 \times 10^{-10}$  mbar. A single-crystal Ag(111) surface was cleaned *in situ* by repeated cycles of Ar<sup>+</sup> ion sputtering followed by annealing to about 900 K. Silicon was evaporated from a heated wafer ( $T \approx 1300$  K) onto the Ag(111) substrate held at 460 K. Hydrogen adsorption was performed by exposing the sample at room temperature to a high-purity H<sub>2</sub> gas (pressures ranging from  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  Pa) cracked by a hot tungsten filament which was heated to about 2000 K. All STM experiments were carried out at 77 K, and the bias voltage was defined as the tip bias with respect to the sample. Density functional theory calculations were performed using projector-augmented wave pseudopotentials in conjunction with the Perdew-Burke-Ernzerhof [18] function and the plane-wave basis set with an energy cutoff at 250 eV. In the calculation, the one-atom-thick silicon film on 5 layers of a ( $4 \times 4$ ) Ag(111) surface with the lattice constant of 11.56 Å were chosen. The vacuum region of more than 15 Å in the

Z direction was applied, which is sufficiently large to eliminate the artificial periodic interaction. All the calculations were performed with the Vienna *Ab Initio* Simulation Package (VASP) [19].

Depending on the substrate temperature and silicon coverage, several monolayer silicene superstructures can be formed on the Ag(111) surface, such as  $(4 \times 4)$ ,  $(\sqrt{13} \times \sqrt{13})R13.9^\circ$  reconstructions with respect to the Ag(111)- $(1 \times 1)$  lattice [20–26], and  $(\sqrt{3} \times \sqrt{3})R30^\circ$  with respect to the Si(111)- $(1 \times 1)$  lattice [21,27–30]. Of these phases, the  $(4 \times 4)$  is the simplest and most well understood one, in which a  $(3 \times 3)$ -Si supercell is placed commensurately with a  $(4 \times 4)$ -Ag supercell. We chose this phase as the model system for hydrogen adsorption. For convenient modeling, we will refer it as  $(3 \times 3)$  with respect to the pristine silicene- $(1 \times 1)$  in the following.

Freestanding silicene- $(1 \times 1)$  is known to consist of two sublattices, *A* and *B*, just as in the case of graphene. But unlike graphene, where the *A* and *B* sublattices are in the same plane, in freestanding silicene these two sublattices are displaced vertically, meaning that Si atoms in one sublattice are all buckled in the same direction, whereas those in the other sublattice are all buckled along the opposite direction [3,7]. When the silicene sheet is placed on an Ag(111) substrate, the buckling configuration of Si atoms is rearranged drastically [21]. Figure 1(a) shows a typical high-resolution STM image of our silicene- $(3 \times 3)$  film, with a characteristic hexagonal arrangement of triangular structures around dark centers. Each  $(3 \times 3)$  unit cell (UC) is composed of two triangular half unit cells (HUC). Figure 1(b) is the structural model, with the red balls indicating upper-buckled Si atoms, which are roughly on top of the Ag atoms. The yellow balls represent lower-buckled Si atoms. Thus, in the total 18 Si atoms in each  $(3 \times 3)$  UC, only six are upper buckled. These six Si atoms correspond to the six protrusions observed in the STM images. They are indeed geometrically higher Si atoms, as has been confirmed by atomic force microscopy [31]. In the upper right of Fig. 1(a), there is a domain boundary area. This area consists of another metastable  $(3 \times 3)$  structure, known as the  $\beta$ - $(3 \times 3)$  phase, which has been reported before [correspondingly, the normal  $(3 \times 3)$  phase is named as  $\alpha$ - $(3 \times 3)$ ] [23,26].

Typical changes induced by the hydrogenation of silicene- $(3 \times 3)$  are illustrated in Fig. 2. Upon exposure of 900 L hydrogen at room temperature, a perfectly ordered structure with the same  $(3 \times 3)$  periodicity can be observed, as shown in Fig. 2(a). Further increasing of the hydrogen dosage does not induce further changes, indicating that the hydrogen adsorption is saturated. A high-resolution image of the hydrogenated structure manifests two inequivalent HUCs, one with six bright spots while the other has only one bright spot in the middle, as shown in Fig. 2(b). The distance between the nearest bright spots is about 3.8 Å, corresponding to the lattice constant of silicene- $(1 \times 1)$ .

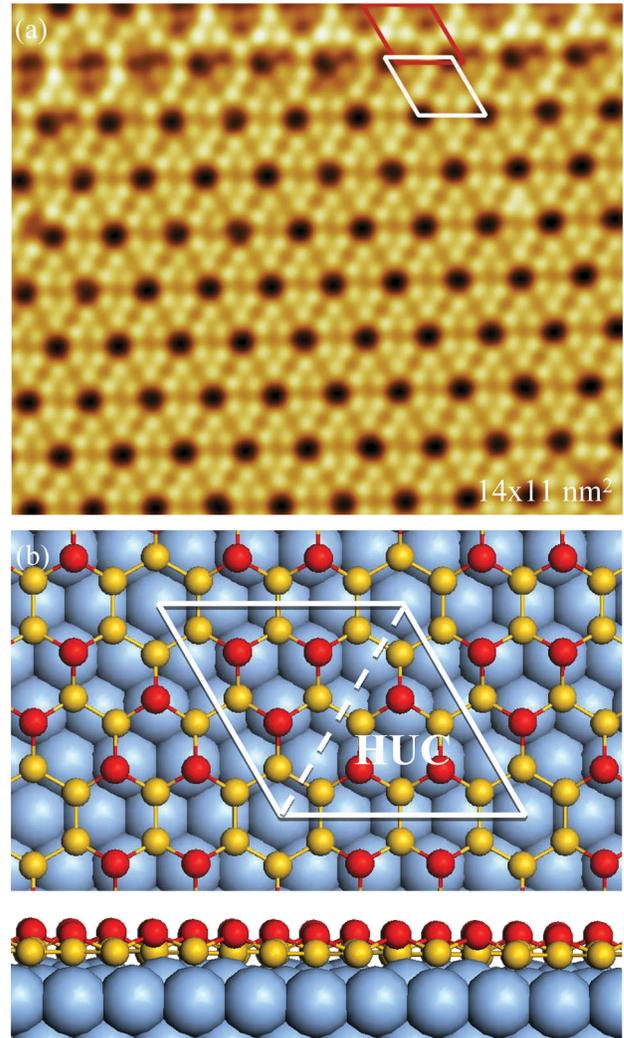


FIG. 1 (color online). STM image and structural model of clean silicene- $(3 \times 3)$  on Ag(111). (a) A typical STM image ( $14 \times 11$  nm) of clean silicene- $(3 \times 3)$ . In the upper-right part of the image, there is a small area consisting of a metastable  $\beta$ - $(3 \times 3)$  phase. The white rhombus marks a  $(3 \times 3)$  unit cell and the red rhombus is the metastable  $\beta$ - $(3 \times 3)$  unit cell. (b) Structural model of silicene- $(3 \times 3)$ . Each unit cell consists of six upper-buckled Si atoms and the two HUCs are mirror symmetric.

It is known that, in silicene, the large Si-Si interatomic distance weakens the  $\pi$ - $\pi$  overlaps, resulting in a low-buckled structure with mixed  $sp^2$  and  $sp^3$  hybridization [32]. The bonding of H on Si is expected to favor  $sp^3$  hybridization, which should increase the out-of-plane buckling of Si in the direction of the bonded hydrogen [33]. Previous theoretical works proposed that a chairlike configuration, with hydrogen atoms attached to *A* and *B* sublattices from the two opposite sides of the silicene sheet, is the most stable for freestanding silicene [14]. However, when taking into account the Ag(111) substrate, only one side of silicene is accessible to hydrogenation. In such a case, the most favorable adsorption site would be the upper-buckled Si atoms. In clean silicene- $(3 \times 3)$ - $\alpha$  on Ag(111),

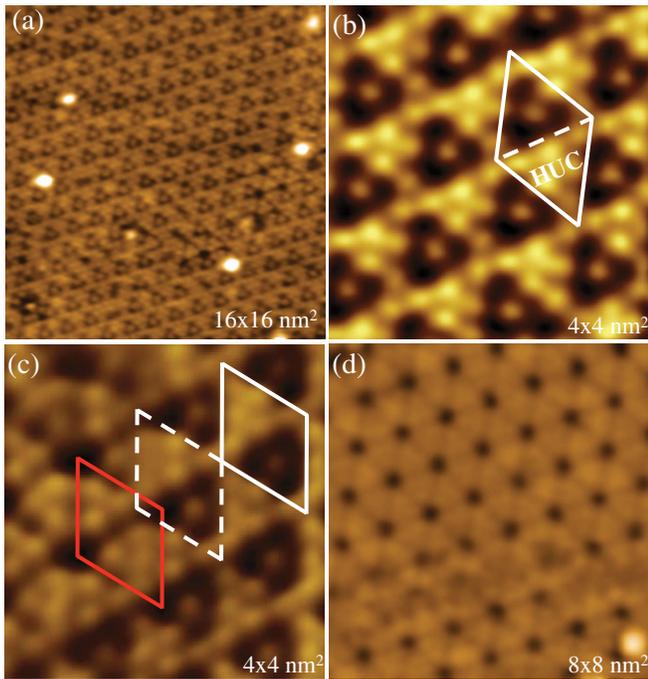


FIG. 2 (color online). (a) A large-area STM image of a hydrogenated silicene- $(3 \times 3)$  surface showing an ordered  $(3 \times 3)$  structure. (b) Enlargement of a STM image of the hydrogenated  $(3 \times 3)$  phase. The white rhombus marks an apparent unit cell of the structure. There are six bright protrusions in one HUC and one protrusion in the other HUC. (c) STM image showing the comparison between the position of apparent UCs of clean and hydrogenated silicene- $(3 \times 3)$ . The red and white rhombuses correspond to clean  $(3 \times 3)$  UC and the hydrogenated  $(3 \times 3)$  UC, respectively. A translation of the white UC (dotted line) does not match the red one. (d) The clean silicene- $(3 \times 3)$  surface is fully recovered after annealing the surface at 450 K.

there are six upper-buckled Si atoms in each UC. Thus naturally we would expect that H atoms be bonded to these six Si atoms. The resulting H-saturated configuration model is shown in Fig. 3(a). However, this model indicates that the two HUCs are mirror symmetric, and both have three protrusions in the simulated STM image illustrated in Fig. 3(b). Note that the STM image looks quite similar to a clean silicene- $(3 \times 3)$  surface. This is because the H bonding simply increases the buckling degree of Si atoms but does not change the general buckling configuration. It is obvious that these features conflict with our experimental observations, indicating that this model could be incorrect.

In order to find out the exact picture for silicene hydrogenation, we refer to an important experimental fact. In a surface that is not fully hydrogenated, we were able to find clean silicene- $(3 \times 3)$  (symmetric HUCs) coexisting with the hydrogenated, symmetry-broken area. An example is shown in Fig. 2(c), where clean silicene- $(3 \times 3)$  is found in the left part of the image whereas the right part is hydrogenated. The apparent unit cells of clean and hydrogenated silicene- $(3 \times 3)$  are indicated by the red and white

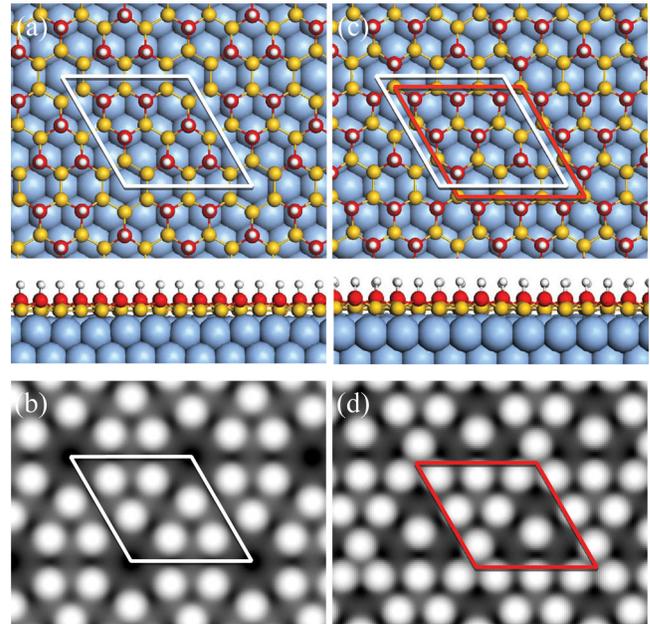


FIG. 3 (color online). (a) and (b) are the structural model and the simulated STM image of a hydrogen-terminated  $\alpha$ - $(3 \times 3)$  model, respectively. (c) and (d) are the structural model and the simulated STM image of a hydrogen-terminated  $\beta$ - $(3 \times 3)$  model, respectively. In (c), the white and red rhombuses correspond to the positions of apparent UCs of  $\alpha$ - $(3 \times 3)$  and  $\beta$ - $(3 \times 3)$  phases, respectively, which are shifted relatively. Note that in (a) and (c), the lateral positions of Si atoms are fixed unchanged and only the buckling configuration has changed, resulting in the change of the position of apparent UCs.

solid rhombuses, respectively, in Fig. 2(c). Surprisingly, the two sets of  $(3 \times 3)$  UCs do not overlap after translation. Instead, they are shifted along Si-Si bond direction by a distance of one Si-Si bond length. There can be only two possibilities. First, the whole silicene film may be laterally shifted. This is, however, unlikely since our monolayer silicene film fully covers the Ag(111) substrate and there is no room for a lateral shift. The second possibility is that the buckling configurations of Si atoms may be changed after hydrogenation, resulting in a shift of the apparent UCs. One possible model of hydrogenated silicene is shown in Fig. 3(c). In this new configuration, the two HUCs are apparently different: one has six upper-buckled Si atoms whereas the other has only one upper-buckled Si atom. Now, if hydrogen atoms adsorb on all the upper-buckled Si atoms, there will be seven protrusions in one unit cell in the simulated STM image, as shown in Fig. 3(d), which are perfectly consistent with experimental STM images. Comparing models 3(a) and 3(c), the lateral position of the whole lattice is fixed unchanged, but the change of buckling configuration results in a shift of the apparent position of the unit cells. Such a shift is exactly what has been observed in our experiments [Fig. 2(c)].

The clean silicene- $(3 \times 3)$ - $\alpha$  has two symmetric HUCs. After hydrogenation, the symmetry is broken, so there can

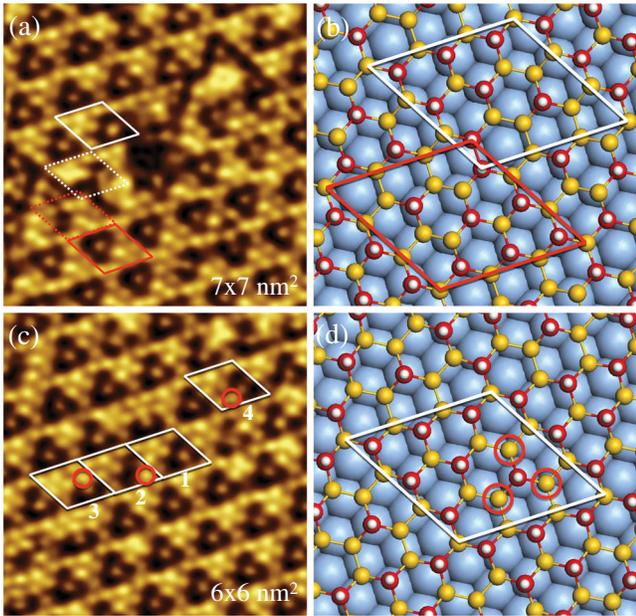


FIG. 4 (color online). (a) STM image of an area with two hydrogenated silicene domains in the upper-left and the lower-right part of the image. The orientations of the black triangles indicate that the two domains are mirror symmetric. (b) The structural model showing unit cells of two mirror-symmetric domains. The red and white rhombuses are relatively shifted along the Si-Si bond direction by a Si-Si bond length. (c) STM image of hydrogenated silicene. Four unit cells are marked by the numbers 1–4. In UCs number 2–4, there is one additional hydrogen atom in the black HUC. (d) Structural model showing the possible adsorption positions of the additional hydrogen atom (red circles).

be two different configurations in hydrogenated silicene- $(3 \times 3)$ . Indeed, we have observed two mirror-symmetric domains in hydrogenated silicene- $(3 \times 3)$  in STM images, as shown in Fig. 4(a). In this image, the orientation of the black triangle for the upper and lower parts of the image is flipped, which can be perfectly explained by the structural model depicted in Fig. 4(b). Note that we observed that the UCs for two configurations, shown by the red and white rhombuses, are also relatively shifted with each other, which is exactly a requirement of the structural model. This provides further support of our structural model.

Interestingly, our hydrogenated silicene structure can be connected with a previously observed metastable  $\beta$  phase of clean silicene- $(3 \times 3)$  [26]. This phase is often observed in boundaries of normal  $(3 \times 3)$  domains, as shown in Fig. 1(a), where strain may play a role in stabilizing this phase. In this phase, the two HUCs are inequivalent: one consists of six protrusions and the other consists of only one protrusion. The structural model of  $\beta$ - $(3 \times 3)$ , proposed by Guo *et al.* [34], is exactly the same as our hydrogenated silicene- $(3 \times 3)$  depicted in Fig. 3(c), if one ignores the hydrogen atoms on top. Similarly, there is a shift of the apparent UC of the  $\beta$ - $(3 \times 3)$  phase as compared with

the  $\alpha$ - $(3 \times 3)$  phase. This can be qualitatively understood as follows: In the clean silicene case, the energy difference between the stable  $\alpha$ - $(3 \times 3)$  and metastable  $\beta$ - $(3 \times 3)$  is small, which is the reason why both phases coexist, although the  $\alpha$ - $(3 \times 3)$  phase is dominating. In hydrogenated silicene, the attachment of H atoms increases the degree of Si buckling and thus increases the strain. So  $\beta$ - $(3 \times 3)$  may become slightly more stable. To confirm this, we performed DFT calculations on the binding energy of hydrogenated  $\alpha$ - $(3 \times 3)$  and  $\beta$ - $(3 \times 3)$ , corresponding to models shown in Figs. 3(a) and 3(c). The results of structural parameters are shown in the Supplemental Material [35]. We compare the total energy of two systems: one with six H atoms adsorbed on  $\alpha$ - $(3 \times 3)$  plus one free H atom, and the other with seven H atoms adsorbed on  $\beta$ - $(3 \times 3)$ . Based on the calculated binding energies, we obtained  $E_b = -17.296$  eV for the former case and  $E_b = -18.674$  eV for the latter case. Thus, the hydrogenated silicene with a  $\beta$ - $(3 \times 3)$  lattice is indeed a bit more stable. In order to distinguish our hydrogenated silicene- $(3 \times 3)$  phase from the clean silicene- $(3 \times 3)$   $\alpha$  and  $\beta$  phases, we call it the  $\gamma$ - $(3 \times 3)$  phase.

We can further understand the adsorption mechanism qualitatively through a sublattice adsorption picture. As proposed previously, H atoms tend to adsorb on the same upper-buckled sublattice of freestanding silicene- $(1 \times 1)$  [15]. However, in clean silicene- $(3 \times 3)$  on Ag(111), the six upper-buckled Si atoms, located separately in two HUCs, belong to different sublattices. So the adsorption of six H atoms on them is not a favorable configuration. In contrast, in our adsorption model, among the seven Si atoms that are bonded with H atoms, six are in the same HUC and belong to the same sublattice, while only the one in the other HUC is in the other sublattice. Therefore our model favors the sublattice adsorption picture. This explanation can be further supported by experimental observation of extra H atoms, as shown in Fig. 4(c). In this image, we mark four different UCs. UC number 1 is a normal UC with seven protrusions. UCs number 2–4 all have an additional protrusion marked by red circles. The position of this extra H nicely corresponds to the three encircled Si atoms shown in Fig. 4(d), which are in the same sublattice as the upper-buckled Si atoms in HUC with six H atoms. These three Si atoms, originally lower buckled, should be easy to be pulled up once there is an extra H attached to them.

Finally, we exploited the dehydrogenation process. It is remarkable that the fully hydrogenated silicene sheet can be completely restored to its original state by annealing the sample to a moderate temperature, about 450 K. As is shown in Fig. 2(d), a regular monolayer silicene- $(3 \times 3)$  structure and domain boundary are completely restored after hydrogen desorption. The adsorption-desorption cycle can be repeated many times without degradation of the silicene film if the UHV system is clean enough. The relative lower desorption temperature is consistent with

the lower binding energy of H on silicene ( $\sim 2.67$  eV per H atom) as compared with that on graphene (6.56 eV per H atom) [10]. In the case of graphene, the desorption temperature is as high as 1100 K [13]. The easily reversible hydrogenation of monolayer silicene suggests that silicene may be useful for controllable hydrogen storage.

In summary, our STM observations and DFT calculations reveal a structural transition resulting from the rearrangement of the buckled Si atoms after hydrogenation. The fully hydrogenated silicene monolayer prefers seven H atoms in one silicene- $(3 \times 3)$  unit cell. By annealing the hydrogenated silicene to about 450 K, dehydrogenation occurs and the surface restores to the initial silicene- $(3 \times 3)$ . Our work provides a comprehensive picture for silicene hydrogenation, and paves the way for further investigation of the electronic properties of hydrogenated silicene, such as band-gap controlling and magnetism that have been predicted by theoretical calculations [14,15].

This work was supported by the MOST of China (Grants No. 2012CB921703, No. 2013CBA01601, and No. 2013CB921702), and the NSF of China (Grants No. 11334011, No. 11322431, No. 11174344, and No. 91121003), and the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDB07020100.

---

\*Corresponding author.  
lchen@iphy.ac.cn

†Corresponding author.  
khwu@iphy.ac.cn

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).
- [2] K. Takeda and K. Shiraishi, *Phys. Rev. B* **50**, 14916 (1994).
- [3] G. G. Guzmán-Verrí and L. C. Lew Yan Voon, *Phys. Rev. B* **76**, 075131 (2007).
- [4] C. L. Kane and E. J. Mele, *Phys. Rev. Lett.* **95**, 226801 (2005).
- [5] 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 (London)* **438**, 197 (2005).
- [6] Y. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim, *Nature (London)* **438**, 201 (2005).
- [7] C. C. Liu, W. Feng, and Y. Yao, *Phys. Rev. Lett.* **107**, 076802 (2011).
- [8] M. Ezawa, *Phys. Rev. Lett.* **109**, 055502 (2012).
- [9] M. Ezawa, *Phys. Rev. Lett.* **110**, 026603 (2013).
- [10] J. O. Sofo, A. S. Chaudhari, and G. D. Barber, *Phys. Rev. B* **75**, 153401 (2007).
- [11] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, *Science* **323**, 610 (2009).
- [12] R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, Z. Slijivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann, and L. Hornekær, *Nat. Mater.* **9**, 315 (2010).
- [13] R. Balog, B. Jørgensen, J. Wells, E. Lægsgaard, P. Hofmann, F. Besenbacher, and L. Hornekær, *J. Am. Chem. Soc.* **131**, 8744 (2009).
- [14] L. C. Lew Yan Voon, E. Sandberg, R. S. Aga, and A. A. Farajian, *Appl. Phys. Lett.* **97**, 163114 (2010).
- [15] F. B. Zheng and C. W. Zhang, *Nanoscale Res. Lett.* **7**, 422 (2012).
- [16] B. Huang, H. X. Deng, H. Lee, M. Yoon, B. G. Sumpter, F. Liu, S. C. Smith, and S. H. Wei, *Phys. Rev. X* **4**, 021029 (2014).
- [17] M. Houssa, E. Scalise, K. Sankaran, G. Pourtois, V. V. Afanas'ev, and A. Stesmans, *Appl. Phys. Lett.* **98**, 223107 (2011).
- [18] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [19] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [20] 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).
- [21] B. Feng, Z. Ding, S. Meng, Y. Yao, X. He, P. Cheng, L. Chen, and K. Wu, *Nano Lett.* **12**, 3507 (2012).
- [22] H. Jamgotchian, Y. Colignon, N. Hamzaoui, B. Ealet, J. Y. Hoarau, B. Aufray, and J. P. Bibérian, *J. Phys. Condens. Matter* **24**, 172001 (2012).
- [23] D. Chiappe, C. Grazianetti, G. Tallarida, M. Fanciulli, and A. Molle, *Adv. Mater.* **24**, 5088 (2012).
- [24] C. L. Lin, R. Arafune, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi, and M. Kawai, *Appl. Phys. Express* **5**, 045802 (2012).
- [25] H. Enriquez, S. Vizzini, A. Kara, B. Lalmi, and H. Oughaddou, *J. Phys. Condens. Matter* **24**, 314211 (2012).
- [26] Z. L. Liu, M. X. Wang, J. P. Xu, J. F. Ge, G. Le Lay, P. Vogt, D. Qian, C. L. Gao, C. Liu, and J. F. Jia, *New J. Phys.* **16**, 075006 (2014).
- [27] L. Chen, C. C. Liu, B. Feng, X. He, P. Cheng, Z. Ding, S. Meng, Y. Yao, and K. Wu, *Phys. Rev. Lett.* **109**, 056804 (2012).
- [28] L. Chen, H. Li, B. Feng, Z. Ding, J. Qiu, P. Cheng, K. Wu, and S. Meng, *Phys. Rev. Lett.* **110**, 085504 (2013).
- [29] L. Chen, B. Feng, and K. Wu, *Appl. Phys. Lett.* **102**, 081602 (2013).
- [30] B. Feng, H. Li, C. C. Liu, T. N. Shao, P. Cheng, Y. Yao, S. Meng, L. Chen, and K. Wu, *ACS Nano* **7**, 9049 (2013).
- [31] A. Resta, T. Leoni, C. Barth, A. Ranguis, C. Becker, T. Bruhn, P. Vogt, and G. Le Lay, *Sci. Rep.* **3**, 2399 (2013).
- [32] C. C. Liu, W. Feng, and Y. Yao, *Phys. Rev. Lett.* **107**, 076802 (2011).
- [33] T. H. Osborn, A. A. Farajian, O. V. Pupyshva, R. S. Aga, and L. C. Lew Yan Voon, *Chem. Phys. Lett.* **511**, 101 (2011).
- [34] Z. X. Guo, S. Furuya, J. I. Iwata, and A. Oshiyama, *Phys. Rev. B* **87**, 235435 (2013).
- [35] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.114.126101> for calculations of the geometry parameters and binding energies of different silicene phases with and without hydrogen adsorption, plus the  $dI/dV$  measurement and DFT calculation of the density of states in hydrogenated silicene.