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Weimin Wang, Weine Olovsson and Roger Uhrberg

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Band structure of hydrogenated silicene on Ag(111): Evidence for half-silicaneW. Wang,^{*} W. Olovsson, and R. I. G. Uhrberg*Department of Physics, Chemistry, and Biology, Linköping University, S-581 83 Linköping, Sweden*

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In the case of graphene, hydrogenation removes the conductivity due to the bands forming the Dirac cone by opening up a band gap. This type of chemical functionalization is of the utmost importance for electronic applications. As predicted by theoretical studies, a similar change in the band structure is expected for silicene, the closest analog to graphene. We here report a study of the atomic and electronic structures of hydrogenated silicene with hydrogen on one side, the so-called half-silicane. The (" $2\sqrt{3} \times 2\sqrt{3}$ ") phase of silicene on Ag(111) was used in this Rapid Communication since it can be formed homogeneously across the entire surface of the Ag substrate. Low-energy electron diffraction and scanning tunneling microscopy data clearly show that hydrogenation changes the structure of silicene on Ag(111) resulting in a (1×1) periodicity with respect to the silicene lattice. The hydrogenated silicene also exhibits a quasiregular $(2\sqrt{3} \times 2\sqrt{3})$ -like arrangement of vacancies. Angle-resolved photoelectron spectroscopy revealed two dispersive bands which can be unambiguously assigned to half-silicane. The common top of these bands is located at ~ 0.9 eV below the Fermi level. We find that the experimental bands are closely reproduced by the theoretical band structure of free-standing silicene with H adsorbed on the upper hexagonal sublattice.

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Silicene is, in analogy with graphene, predicted to have a band structure forming a Dirac cone (occupied by massless fermions) with the apex at the Fermi level. Two-dimensional (2D) materials with this kind of exceptional band structure are of great interest for various electronic applications [1–3]. This requires, however, different kinds of functionalization. Adsorption of hydrogen atoms is one method which is of great interest since theoretical studies show that it leads to an opening of a band gap which is crucial for applications in future nanoelectronic devices [4]. An experimental determination of the band structure of hydrogenated silicene is therefore of utmost importance. Silicene is mostly synthesized on Ag(111) substrates because of a low Si-Ag intermixing and a “matching” 3 to 4 ratio between the lattice constants of silicene and the Ag(111) surface [5]. After many years of silicene studies, experimental evidence of a Dirac cone is still missing. As suggested by theoretical calculations, the absence of Dirac fermions is due to strong hybridization between Si and Ag atoms [6]. Even though Dirac cones have not been experimentally observed, a silicene field-effect transistor was recently reported using (4×4) and (" $2\sqrt{3} \times 2\sqrt{3}$ ") silicene grown on a Ag(111) thin film on mica [7]. This paper has shown the great potential of silicene in nanoelectronic devices. This emphasizes the importance of the functionalization of graphenelike 2D materials, a topic which we address here by reporting the atomic and electronic structure of hydrogenated silicene.

In this Rapid Communication, hydrogenation of (" $2\sqrt{3} \times 2\sqrt{3}$ ") silicene on Ag(111) has been studied by low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and angle-resolved photoelectron spectroscopy (ARPES). LEED patterns show that the hydrogenation changes the structure of the silicene sheet to essentially a (1×1) structure with some higher-order periodicity indicated by weak additional diffraction spots. STM images of the

hydrogenated silicene reveal a hexagonal structure with the periodicity of the silicene (1×1) lattice and vacancies with a quasi- $(2\sqrt{3} \times 2\sqrt{3})$ periodicity. The ARPES data show two dispersive bands around normal emission which are in good agreement with the theoretical band structure, calculated for a half-silicane model with hydrogen adsorbed on one of the two hexagonal sublattices of free-standing silicene.

Samples were prepared *in situ* in two separate ultrahigh vacuum (UHV) systems, one equipped with LEED/STM and the other with LEED/ARPES. In the UHV system with the STM, the parameters for forming half-silicane were investigated which resulted in the following preparation procedure. A clean Ag(111) surface was prepared by repeated cycles of sputtering by Ar^+ ions (1 keV) and annealing at approximately 400 °C until a sharp (1×1) LEED pattern was obtained. About one monolayer (ML) of Si was deposited at a rate of ~ 0.03 ML/min whereas the Ag(111) substrate was kept between 280 and 300 °C. This type of preparation repeatedly results in a full coverage of (" $2\sqrt{3} \times 2\sqrt{3}$ ") silicene on Ag(111) as reported in Ref. [8]. After a quality check by LEED and STM, the (" $2\sqrt{3} \times 2\sqrt{3}$ ") silicene was exposed to atomic hydrogen generated by dissociating H_2 molecules at a hot W filament (1800 °C) placed ~ 6 cm in front of the sample. The exposures were quantified during the experiments in terms of the number of langmuirs (L) of H_2 molecules ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$). STM images were recorded at room temperature using an Omicron variable temperature STM in a UHV system at Linköping University which was also equipped with a LEED optics. ARPES data and LEED patterns were obtained at the MAX-lab synchrotron radiation facility using the end station at beamline I4. ARPES data were measured on samples prepared using the same parameters and procedures as in the LEED/STM system. All spectra were acquired at room temperature by a Phoibos 100 analyzer from Specs with a two-dimensional detector. The energy and angular resolutions were 50 meV and 0.3° , respectively. First-principles density functional theory calculations were performed using the full potential linearized augmented plane-wave method as

^{*}Corresponding author: weiwa49@ifm.liu.se

FIG. 1. (a) Typical LEED pattern (77 eV) of (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) silicene on Ag(111) showing diffraction from the two possible silicene orientations rotated by $+10.9^\circ$ and -10.9° compared to Ag(111), respectively. Some of the diffraction spots originate from the moirélike long-range order observed by STM, see Fig. 2(a). For a detailed assignment of the diffraction spots see Ref. [8]. (b) Typical LEED pattern (82 eV) of the (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) silicene surface exposed to atomic hydrogen. The arrows indicate a Ag (1×1) diffraction spot and two diffraction spots $\text{Si}^{(1)}$ and $\text{Si}^{(2)}$ from the two rotated silicene sheets, respectively.

implemented in the WIEN2K package [9]. The positions of the atoms were fully relaxed using the projector augmented-wave method Vienna *ab initio* simulation package code [10]. For free-standing half-silicene, the energy cutoff of the plane-wave basis set was 375 eV, and the k -point mesh was $9 \times 9 \times 1$. All calculations employed the generalized gradient approximation for exchange and correlation, according to Perdew *et al.* [11].

Silicene synthesized on Ag(111) can form various phases, such as (4×4) , $(\sqrt{13} \times \sqrt{13})$, and (“ $2\sqrt{3} \times 2\sqrt{3}$ ”). It has been experimentally verified that the (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) phase can cover the whole surface without the coexistence of any other phases [8,12]. Hence, the (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) phase is well suited for a study of the properties of hydrogenated silicene. Before hydrogenation, the quality of the as-prepared (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) silicene was confirmed by LEED and STM to match the silicene in our previous paper [8]. Figure 1(a) shows a typical LEED pattern of (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) silicene on Ag(111). During hydrogenation, there is a charge transfer occurring from Si atoms to H atoms. The hybridization changes from mixed sp^2/sp^3 to sp^3 hybridization [13]. After exposure to atomic hydrogen, the LEED pattern in Fig. 1(b) shows clear changes. Some of the higher-order diffraction spots are absent whereas the others are significantly weaker. In contrast, the silicene (1×1) spots are brighter. The LEED pattern in Fig. 1(b) is dominated by diffraction from the two differently oriented silicene sheets, indicated by $\text{Si}^{(1)}$ and $\text{Si}^{(2)}$. In a subsequent investigation, we found that the quenched and the diminished spots can be brought back by annealing at 270°C for a short time (~ 5 min), which shows that the process of hydrogenation on silicene is more easily reversible than on graphene [14]. After an extended exposure (approximately six times saturation exposure) the LEED pattern shows only (1×1) Ag spots (not shown in the Rapid Communication), and annealing cannot bring back diffraction spots from silicene anymore. Based on a theoretical study, hydrogenation of the silicene layer on Ag(111) is a

FIG. 2. (a) Atomically resolved empty state STM images of a $14.2 \times 14.2 \text{ nm}^2$ area of (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) silicene on Ag(111). (b) A $12.3 \times 12.3 \text{ nm}^2$ area of half-silicene formed by atomic hydrogen exposure (saturation exposure, 150 L), showing a hexagonal pattern corresponding to a (1×1) periodicity of silicene and vacancies (dark) arranged in a quasiperiodic fashion. There are also larger bright protrusions in the STM image after the hydrogenation. (c) A $4.3 \times 4.3 \text{ nm}^2$ area of hydrogenated silicene. The (1×1) periodicity is indicated by a green diamond, and red diamonds illustrate the ($2\sqrt{3} \times 2\sqrt{3}$) cell with respect to Ag(111), i.e., $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ with respect to silicene. The ($2\sqrt{3} \times 2\sqrt{3}$) cells in (b) and (c) describe the part where the vacancies are ordered. All STM images were recorded at room temperature in constant current mode with a tunneling current of 200 pA and a sample bias of +1.0 V for (a) and +50 mV for (b) and (c).

self-limited process [15]. A H coverage of 50% was reported to be energetically favorable. For continued hydrogenation, the hydrogen atoms were predicted to adsorb on both sides of the silicene layer, leading to a detachment of the silicene layer from the Ag(111) surface. This could explain why there was no sign of any Si-related diffraction after the extended hydrogen exposure.

Information about the morphology of the initial silicene and the half-silicene formed by hydrogenation was obtained by STM. The atomically resolved filled state STM image in Fig. 2(a) shows the structure of (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) silicene on Ag(111) with a typical moirélike long-range pattern of bright honeycombs. Between the bright regular honeycombs there are distorted honeycombs. Both the regular and the distorted honeycombs have very consistently been reported in the literature for (“ $2\sqrt{3} \times 2\sqrt{3}$ ”) silicene [16,17]. Our previous work [8] confirms that this silicene phase covers the

FIG. 3. (a) SBZs of (1×1) Ag(111) (blue), $(2\sqrt{3} \times 2\sqrt{3})$ reconstruction (black), and two (1×1) half-silicane SBZs rotated by $\pm 10.9^\circ$ (green). (b) ARPES data from half-silicane obtained at a photon energy of 26 eV along $\bar{\Gamma} \rightarrow \bar{M}_{\text{Ag}}$ and $\bar{\Gamma} \rightarrow \bar{K}_{\text{Ag}}$ of the Ag (1×1) SBZ. Note that these paths probe equivalent $k_{\parallel}$ lines of the $\pm 10.9^\circ$ half-silicane SBZs. The energy range of the ARPES data extends down to a binding energy of 3.5 eV. Below that energy there is intense emission from the Ag $4d$ bands, and no useful information of the half-silicane bands can be obtained. S_1 and S_2 are two dispersive bands which originate from half-silicane. The label Ag- sp indicates Ag bulk emission and U- sp points at dispersive features due to umklapp scattering of the Ag- sp emission by $(2\sqrt{3} \times 2\sqrt{3})$ reciprocal lattice vectors. (c) Top and side views of a half-silicane model with hydrogen adsorbed on one of the two hexagonal sublattices of free-standing silicene. The green diamond represents the (1×1) silicane unit cell, and blue and pink balls represent Si and H atoms, respectively. The bond length between Si and H atoms is 1.52 Å, and the Δz of the two Si sublattices is 0.68 Å. (d) Calculated band structure of the half-silicane model in (c). The dashed line indicates the binding energy limit of the ARPES measurement, relative to the top of the Σ_1 and Σ_2 bands at $\bar{\Gamma}$.

whole surface with a specific buckling for which only 2 out of the 14 Si atoms per $(2\sqrt{3} \times 2\sqrt{3})$ unit cell are observed by STM. After hydrogenation, the structure is completely changed. The half-silicane shows a (1×1) periodicity with a quasiperiodic arrangement of defects as shown by Figs. 2(b) and 2(c). The green diamond corresponds to a silicene (1×1) periodicity, and the red diamonds correspond to a $(2\sqrt{3} \times 2\sqrt{3})$ periodicity with respect to the Ag(111) lattice, i.e., $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ with respect to silicene. The STM images indicate that every second Si atom of the silicene layer is bonding to a hydrogen atom resulting in the hexagonal structure. As a consequence of the hydrogenation, the complicated buckling of the initial “ $2\sqrt{3} \times 2\sqrt{3}$ ” silicene has been removed.

It is interesting to note that hydrogenation of “ $2\sqrt{3} \times 2\sqrt{3}$ ” silicene results in a (1×1) periodicity, whereas hydrogenation of (3×3) silicene [(4×4) with respect to Ag(111)] resulted in a modified (3×3) structure as reported in Ref. [18].

The defects, which appear darker than the hydrogen terminated Si atoms, are most naturally interpreted as vacancies. It is intriguing to find a quasiperiodic ordering of these vacancies.

Locally, the defects are found to form a $(2\sqrt{3} \times 2\sqrt{3})$ structure as indicated by the red unit cell in Fig. 2(b). These vacancies are interpreted by Qiu *et al.* [12] as missing H atoms. In our study, we found that increasing hydrogen exposures do not decrease the density of the vacancies but start to remove Si atoms. After 1.33 times the saturation exposure, we found areas where Si had been removed showing bare Ag(111). An alternative explanation to the presence of vacancies could be that Si atoms are actually removed from the silicene sheet during hydrogenation. It is here interesting to note that our study and that of Qiu *et al.* show bright protrusions of similar size and density (number/area). In Ref. [12] these protrusions were assigned to contamination during the H exposure. It is, however, not very likely that our and their experimental conditions would result in “identical” contamination effects. We therefore regard the bright protrusions as features that arise naturally from the hydrogenation process. A plausible explanation would be that the bright protrusions are small clusters formed by Si atoms that have been removed from the silicene layer, each leaving a vacancy behind (see the Supplemental Material [19]). This speculation needs, however, further confirmation.

ARPES was performed along the $\bar{\Gamma} \rightarrow \bar{M}_{\text{Ag}}$ and $\bar{\Gamma} \rightarrow \bar{K}_{\text{Ag}}$ directions of the (1×1) surface Brillouin zone (SBZ) of Ag(111) as illustrated by the black arrows in Fig. 3(a). Apart from dispersive features from the Ag(111) substrate (Ag-*sp* and U-*sp*), there are two clear bands S_1 and S_2 , which can be conclusively assigned as half-silicane. They show good agreement with the calculated bands of free-standing half-silicane in Fig. 3(d), even though the band mapping directions are 10.9° off the high-symmetry lines of the half-silicane SBZs. The directions used for the band mapping are equivalent for the two orientations of the half-silicane domains, and they were chosen deliberately to avoid the complexity of two superimposed half-silicane band structures in the ARPES data. We also mapped the band structure along a direction corresponding to a symmetry line for one of the half-silicane orientations. Such a line corresponds to a path that is 21.8° off the symmetry direction for the other half-silicane orientation. The bands around normal emission did not show any noticeable difference, but for large emission angles, the S_1 bands originating from each of the two half-silicane orientations were observed (see the Supplemental Material [19]). There are two differences between the ARPES data and the calculated band structure of free-standing half-silicane. One is that the calculation locates Σ_1 and $\Sigma_2 \sim 0.3$ eV higher in energy than the experimental half-silicane bands S_1 and S_2 . Another difference is that Σ_3 is not observed in the ARPES data. Σ_3 is a half-filled band formed by p_z orbitals originating mainly from Si atoms without H. These atoms belong to the silicene sublattice that is closest to the Ag(111) surface. In

the experiment, the half-silicane is supported by the Ag(111) surface, and a hybridization with Ag orbitals might be the reason why we do not observe the weakly dispersive Σ_3 band around the Fermi level.

In conclusion, our LEED and STM observations show clearly that the hydrogenation changes the structure of the (" $2\sqrt{3} \times 2\sqrt{3}$ ") silicene on Ag(111). The resulting structure corresponds to half-silicane which exhibits a hexagonal structure with a (1×1) periodicity with respect to the silicene lattice. In addition, the half-silicane layer shows a quasiperiodic $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ vacancy pattern which we interpret as missing Si atoms. The ARPES data from the hydrogenated silicene show two dispersive bands which we could unambiguously assign to half-silicane bands by the very good agreement with the calculated band structure of the free-standing half-silicane, i.e., silicene with H adsorbed on one side. This report of the electronic properties of half-silicane is important for future applications in Si-based electronics.

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