Effects of Oxygen Adsorption on the Surface State of Epitaxial Silicene on Ag(111)

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Epitaxial silicene, which is one single layer of silicon atoms packed in a honeycomb structure, demonstrates a strong interaction with the substrate that dramatically affects its electronic structure. The role of electronic coupling in the chemical reactivity between the silicene and the substrate is still unclear so far, which is of great importance for functionalization of silicene layers. Here, we report the reconstructions and hybridized electronic structures of epitaxial 4 × 4 silicene on Ag(111), which are revealed by scanning tunneling microscopy and angle-resolved photoemission spectroscopy. The hybridization between Si and Ag results in a metallic surface state, which can gradually decay due to oxygen adsorption. X-ray photoemission spectroscopy confirms the decoupling of Si-Ag bonds after oxygen treatment as well as the relatively oxygen resistance of Ag(111) surface, in contrast to 4 × 4 silicene [with respect to Ag(111)]. First-principles calculations have confirmed the evolution of the electronic structure of silicene during oxidation. It has been verified experimentally and theoretically that the high chemical activity of 4 × 4 silicene is attributable to the Si p_z state, while the Ag(111) substrate exhibits relatively inert chemical behavior.

Silicene, one single layer of silicon atoms packed in a honeycomb structure, has been predicted to be a new two-dimensional (2D) Dirac-fermion material.1–3 The electrons in silicene behave as massless charge carriers that can exhibit transport at ultra-fast velocity, due to the linear energy-momentum dispersion relation at the Dirac point.1–3 Strong spin-orbital coupling makes silicene a promising candidate material for the quantum spin Hall effect (QSHE), and it is compatible with current Si-based device technologies. To date, epitaxial growth is the only method that can produce silicene on certain metal substrates.2–4 The electronic structure of such epitaxial silicene is therefore significantly modified by a strong coupling with the substrate, which may annihilate silicene’s Dirac-fermion characteristics.2–4 On the other hand, epitaxial silicene in different superstructures may show various exotic physical and chemical properties due to new surface states that result from hybridization between Si and the metal substrate. For example, density functional theory (DFT) calculations have suggested that in 4 × 4 silicene [with respect to Ag(111)] on Ag(111), wave functions derived from the Si 3p orbitals are delocalized into the substrate. The strong coupling, accompanied by the charge transfer from the substrate to the silicon, breaks the symmetry to modulate the band structure of 4 × 4 silicene. Consequently, a surface metallic band was observed in 4 × 4 silicene on Ag(111) by angle resolved photoemission spectroscopy (ARPES).6 This metallic band would lead to higher chemical reactivity of silicene in comparison to graphene, especially on the surface rather than the edges, which potentially facilitates functionalization of silicene. The chemical properties associated with such a hybrid electronic state in 4 × 4 silicene are still unclear, however, which is an obstacle to potential applications.

Oxygen adatoms can be used to probe and modulate local electronic states at the atomic level in 2D materials via the adsorption process, due to their high chemical activity. In graphene, it is well accepted that the local electronic structure can be tuned from the zero-gap state to a semiconducting state by changing the oxygen dose and the adsorption site of oxygen adatoms.8,9 The interaction between oxygen adatoms and carbon atoms can reflect the intrinsic electronic properties of graphene. Similarly, silicene possesses high chemical reactivity to oxygen, which offers a feasible way to investigate its surface electronic structures by using the oxygen adatom as a
chemical probe. The hybrid surface metallic state in \(4 \times 4\) silicene on Ag(111) would be perturbed by oxygen adatoms via the formation of covalent bonds between oxygen and silicon (or silver). Modulation of electronic states in silicene by oxygen adatoms is also expected, which is critical for the development of electronic devices.

In this work, we report the effects of oxygen adsorption on the surface state of epitaxial \(4 \times 4\) silicene on Ag(111), as determined by scanning tunneling microscopy (STM) and ARPES at the atomic level. The hybridized surface metallic state is found to be highly sensitive to oxygen adatoms. It is revealed that the Shockley surface state on Ag(111) can be revived after the silicene is oxidized. Density functional theory (DFT) calculations indicate that the high chemical reactivity of \(4 \times 4\) silicene originates from the Si \(p_z\) state, which is in good agreement with the experimental results.

**Results**

Figure 1 shows \(15 \times 15\) nm\(^2\) STM topographical images of the Ag(111) surface and a \(4 \times 4\) silicene monolayer epitaxially grown on the substrate. Quantum-interference patterns are clearly visible on the Ag(111) surface, as shown in Figure 1(a). Electrons in the two-dimensional surface states can be scattered by surface point defects, leading to periodic spatial oscillations of the electronic local density of states (LDOS)\(^{13}\). The LDOS can be used to identify a 2D electron gas, because interference will be observed if the 2D electron wave travels towards a scattering defect and encounters the backscattered wave\(^{14}\). In Figure 1(a), the quantum-interference pattern with a period of several tens of angstroms reflects the nature of the 2D electron wave\(^{14}\). In Figure 1(b), the quantum-interference pattern with a period of several tens of angstroms reflects the nature of the 2D electron wave\(^{14}\).

Figure 1(a) inset, a gapped electronic state was identified in scanning tunneling spectroscopy (STS) measurements carried out at oxygen adatom sites on the silicene layer. The surface metallic band is therefore tuned to a semiconducting-like characteristic. When the oxygen dose is increased up to 600 L, the silicene layer is oxidized and forms a disordered structure, as shown in Figure 1(d). Some areas of bare Ag(111) substrate were exposed. Interestingly, the QPI pattern again appears on the Ag(111) surface with the same oscillating period as observed on clean Ag(111) surfaces before the growth of silicene, indicating that Ag(111) substrate acts as an inert material compared to \(4 \times 4\) silicene in the process of oxidization.

Figure 2 shows the ARPES results on occupied states along the \(\Gamma-M_{\text{Ag}}\) and \(\Gamma-K_{\text{Ag}}\) directions of \(4 \times 4\) silicene/Ag(111) before and after oxidization. ARPES was conducted in order to reveal the details of the surface electronic structures, as well as the origin of the electronic hybridization between the silicene and the Ag(111) substrate. Figure 2(d) shows the reciprocal space Brillouin zones (BZ) of \(1 \times 1\) Ag(111) (blue hexagon), free-standing silicene (dashed red hexagon), and \(4 \times 4\) epitaxial silicene with respect to Ag(111) (3 \times 3 silicene with respect to \(1 \times 1\) silicene) (orange hexagons). Note that the \(M_{\text{Ag}}\) and \(K_{\text{Ag}}\) points of Ag(111) coincide with the \(S_{\text{Si}}\) and \(K_{\text{Ag}}\) points of \(4 \times 4\) silicene in the BZ. Figure 2(a) displays the Shockley surface state (SSS) of Ag(111) substrate at the BZ center \(\Gamma\) point (\(k = 0\) \(\text{Å}^{-1}\)). The SSS arises primarily from surface states of nearly free electrons and is associated with the special boundary conditions introduced by the metal/vacuum interface\(^{15}\). The typical bulk \(sp\)-band of Ag lies across the Fermi level\(^{11}\) at \(k = 1.15\) \(\text{Å}^{-1}\). As the coverage of silicene increases, the SSS and \(sp\)-band of Ag become faint, and the SSS eventually disappears when the Ag(111) surface is fully covered by the silicene layer, as shown in Figure 2(b). The weak Ag \(sp\)-band is still observable, which indicates that this band remains stable upon Si deposition. There is a clear new \(\Gamma\)-\(\text{Si}\)-shaped state with a top point at the \(M_{\text{Ag}}\) point. As shown in Figure 2(e), the \(\Gamma\)-\(\text{Si}\)-shaped state along the \(\Gamma-K_{\text{Ag}}\) direction exhibits a variation, where the band traverses the Fermi surface at the \(K_{\text{Ag}}\) (\(S_{\text{Si}}\)) point. The results of band structures along both the \(\Gamma-M_{\text{Ag}}\) and \(\Gamma-K_{\text{Ag}}\) directions are consistent with previous reported works\(^{1}\), indicating that the \(\Gamma\)-\(\text{Si}\)-shaped state is attributable to a hybridization of Si and Ag orbitals that resembles the \(\pi\)-band dispersion in graphhene1. The apex of the state at \(k = 1.28\) \(\text{Å}^{-1}\) in Figure 2(b) is about 0.15 eV below the Fermi level, which is the saddle point of the surface state and at the middle point between two adjacent \(K_{\text{Ag}}\) (\(S_{\text{Si}}\)) points. It should be noted that this feature is absent in the clean Ag(111) spectra and has
been associated with a Ag(111)-related surface band that appears only after Si deposition. In recent studies, a different superstructure of silicene, namely, the $\sqrt{3} \times \sqrt{3}$ reconstruction with respect to $1 \times 1$ silicene, was formed as a second layer on $4 \times 4$ silicene grown on Ag(111) substrate. The predicted Dirac cone has been observed in the $\sqrt{3} \times \sqrt{3}$ silicene$^{18,19}$, which demonstrates that $\sqrt{3} \times \sqrt{3}$ silicene is a true 2D Dirac-fermion material. Both ARPES and STS measurements indicated a strong electron doping (n-type) effect in multilayer $\sqrt{3} \times \sqrt{3}$ silicene evoked by the Ag(111) substrate.$^{18}$ Consequently, the Fermi level in multilayer silicene is lifted by about 0.3 eV, even though there is no hybridized state that can be observed. Thus, the electronic structure of monolayer $4 \times 4$ silicene is completely different from that of multilayer $\sqrt{3} \times \sqrt{3}$ silicene. High surface chemical activity would be expected in $4 \times 4$ silicene because the metallic HSB in $4 \times 4$ silicene leads to a lower work function compared with $\sqrt{3} \times \sqrt{3}$ silicene. In order to confirm the influence of oxygen adatoms on the hybridization between Ag(111) and $4 \times 4$ silicene, a detailed X-ray photoelectron spectroscopy (XPS) characterization of the chemical bonds in the samples was carried out. Figure 3(a) and (b) shows Ag 3d core level XPS spectra for $4 \times 4$ silicene deposited on an Ag(111) sample before and after oxygen treatment, respectively. The experimental data points are displayed with black dots, while the fitted curves are red lines. For the bare Ag(111) substrate, the Ag 3d$_{5/2}$ and 3d$_{3/2}$ peaks at 371.5 eV and 365.5 eV have originated from Ag-Si bonds. A downward energy shift ($\sim$0.7 eV) for the Ag 3d orbital is observed after the deposition of silicene, where the Ag-Si chemical bond forms, indicating that the chemical activity of silicene is higher than for the pure Ag-Ag bond arising from Ag$^6$. Peak splitting of the Ag 3d line was observed after the exposure to 600 L oxygen in Figure 3(b). The peaks could be decomposed in two contributions, coming from the Ag-Ag bond component and the Ag-Si bond component, respectively. The dramatic fall in intensity of Ag-Si and the recovery of Ag-Ag bonds make it manifest that Ag-Si bonds are broken after the oxygen treatment. Moreover, no Ag-O chemical
structure is present in the XPS spectrum, which implies that oxygen adatoms most likely only form bonds with silicon atoms, which supports the resurgence of QPI patterns on Ag(111) after oxidation, as shown in Figure 1(d). Figure 3(c) and (d) shows Si 2p core level spectra for the sample before and after oxygen treatment, respectively. The fitting results for the Si 2p line, as shown in Figure 3(c), make it clear that there are two groups of bonding components, labelled as Si1 and Si2, respectively. The energy gap of the two peaks in each group is a constant value, indicating that the two fitting peaks in one group are related to two Si 2p3/2 and 2p1/2 peaks, respectively. The Si2 peaks at a binding energy around 98.8 eV are related to the Si-Si in silicene, consistent with the previous report 22. The Si1 group is attributed to Si-Ag bonding, since there are no other elements induced in the process of deposition, combined with the fitting results on Ag-Si bonding in Figure 3(a) and (b). The Si-O peaks clearly present after oxygen treatment. The binding energy value (101.6 eV) is lower than the peak position of SiO2-like binding energy (102.3 eV)23, indicating that the valence states of Si-O bonds are lower than Si4+. Therefore, silicene was not fully oxidized to SiO2, which is consistent with previous reports 24 in which the oxygen adatoms are the most energetically favored on the surface of silicene. The intensity of the peaks related to the Si-Ag bonds is significantly reduced with the emergence of the Si-O peak. The variation of the peak intensity demonstrates that oxygen adatoms prefer to decouple the Si-Ag bonds rather than the Si-Si bonds. The XPS results are in a good agreement with our STM and ARPES results, and confirm the decoupling of Si-Ag bonds after oxygen treatment, as well as the relatively high oxygen resistance of the Ag(111) surface, in contrast to 4 × 4 silicene.

Finally, we carried out density functional theory (DFT) calculations to investigate the revived SSS on Ag(111) and to confirm the origins of the VB in silicene oxide, as shown in Figure 4. The first step in our calculation was to determine the superstructure of silicene grown on Ag(111). One layer of silicene was put on top of 5 layers of 4 × 4 Ag(111). The simulated structure shows the same reconstruction as in our STM results, as displayed in Figure 4(a). The Ag d-state and the Si p-state make the heaviest contributions to the density of states (DOS) at the Fermi level (EF), which indicates that the metallic HSB is indeed contributed by the pz electrons of Si atoms and the 4d electrons of the Ag(111) substrate. We then put 0.5 monolayer (ML) oxygen on the stabilized silicene surface. After running molecular dynamics for 7 ps, all the singly coordinated Si atoms have moved to bridge sites, indicating that there is an energy barrier that needs to be overcome for the other O atoms to move to more highly coordinated sites on silicene. Meanwhile, the Si atomic layer becomes disordered, demonstrating that the silicene oxide layer has started to decouple from the underlying Ag(111) substrate. The disordering of the Si overlayer induced by oxygen adatoms is in excellent accordance with the STM observations on the disordered nature of silicene oxide. Figure 4(c) shows the calculated DOS on 4 × 4 silicene covered by 0.5 ML oxygen. The deep level (<2 eV) is mainly contributed by Ag d-states. The DOS near EF, however, consists of Ag, Si, and O orbitals, as shown in the inset of Figure 4(c). It should be pointed out that the Si 3p states and O 2p states form a new band below EF, although Si and O also contribute some partial DOS at EF. The top of this band is at ~0.4 eV, which matches well with the asymmetric band (~0.6 eV) shown in the ARPES results [Figure 2(c, f)]. Thus, we confirmed that this shallow band is the VB of partially...
approximately 0.7 eV, which is much smaller than the binding energy for further functionalization of epitaxial silicene layers. The binding energy to 
chemically react towards oxygen, which is expected to be utilized to 
form Si-O-Si bonds at bridge sites in the 4 × 4 silicon surface. Red, yellow, and blue balls in (b) and (d) represent oxygen, silicon, and silver atoms, respectively.

Discussion
As mentioned above, 4 × 4 silicon on Ag(111) demonstrates high chemical reactivity towards oxygen, which is expected to be utilized to further functionalize epitaxial silicon layers. The binding energy between the epitaxial silicon layer and the Ag(111) surface is approximately 0.7 eV, which is much smaller than the binding energy for Si-O (between 4.0 and 12.0 eV). The oxygen thus tends to bond firstly with Si atoms in the silicon instead of Ag atoms in the substrate. Moreover, the energy required for oxygen adsorption on Ag(111) is much higher than on the Si surface with dangling bonds (p orbital), and therefore, bare Ag(111) surface but not silver oxide in the fully oxidized silicon sample. Due to the characteristic sp2 hybridization of Si, energetically stable Si-O-Si bonds would be expected when silicon is exposed to a high oxygen dose (600 L). The Si-O bond length in oxidized 4 × 4 silicon on Ag(111) is between 1.63 Å and 1.67 Å, as derived from our DFT calculations, which is somewhat smaller than the bond length of about 1.70 Å in SiO2. Consequently, the silicon layer crumples during oxidation, resulting in some “silicene-free” areas. Our theoretical and experimental results also suggest that the silicene oxide layer could possibly detach from the Ag(111) substrate and form quasi-free-standing nanosheets. By analogy with graphene, it is proposed that reducing these quasi-free-standing nanosheets may offer a feasible way to obtain freestanding silicon nanosheets [or reduced silicene oxide (RSO)].

In conclusion, we have investigated the oxidation effects on the structure and electronic properties of 4 × 4 silicon on Ag(111). After oxidation, the silicene oxide exhibits a disordered structure with a semiconductor-like band structure. By combining DFT calculations and ARPES results, it is verified that the 2D metallic surface state in 4 × 4 silicon on Ag(111) is attributable to hybridization of Si p and Ag d states. The hybridization is broken and the Ag(111) Shockley surface state can be revived when the silicene is oxidized. This surface band demonstrates high chemical activity, which will facilitate chemical functionalization of silicon layers.

Methods
Sample preparation. The silicon layers were grown on Ag(111) substrate by the deposition of silicon from a heated silicon wafer in a preparation chamber attached to a low temperature (LT)-STM system under ultra-high vacuum (UHV, <5 × 10⁻¹¹ torr). A clean Ag(111) substrate was prepared by Ar⁺ sputtering following by annealing at 550 °C for several cycles. The deposition flux of Si was 0.08 monolayers per minute (ML/min). The temperature of the Ag(111) substrate was kept at 220 °C during deposition. Oxygen molecules were introduced onto the silicon surface by a leak valve. The Langmuir (L) is used as the unit of exposure of O2, i.e. 1 L is an exposure of 10⁻¹² torr O2 in one second.

STM and STS characterizations. The STM and STS measurements were carried out on an ultra-high vacuum (UHV) LT-STM system (SNOM1400, Unisoku Co.) in UHV (<8 × 10⁻¹¹ torr) at 77 K. STS differential conductance (dI/dV) (where I is current and V is voltage) measurements were conducted with lock-in detection by applying a small modulation of 20 mV to the tunnel voltage at 973 Hz. Before STS measurements, the Pt/Ir tip was calibrated on a silver surface.

ARPES and X-ray photoemission spectroscopy (XPS) characterizations. In-situ ARPES and XPS characterizations were performed at a photoelectron spectroscopy station in the Beijing Synchrotron Radiation Facility (BSRF) using a SCIENTA R4000 analyzer. A monochromatized He I light source (21.2 eV) was used for the band dispersion measurements. The total energy resolution was set to 15 meV, and the angular resolution was set to ~0.3°, which gives momentum resolution of ~0.01 Å⁻¹. The XPS experiments were performed at Beamline 4B9B, and the variable photon energies used were referenced to a fresh Au polycrystalline film. Photons at 700 eV, 500 eV, and 180 eV were used to excite the Ag 3d and Si-2p electrons in the samples, and the total energy resolutions were about 0.4 meV, 0.3 meV, and 0.15 meV, respectively. All the XPS data are fitted using the XPS Peak 4.1 software package. All the background subtraction was calculated by the “Shirley + Linear” background approach. All the XPS peaks were fitted by Gaussian-Lorentzian functions. The silicon samples used in the ARPES and XPS characterizations were prepared under the same conditions as for the STM and STS characterizations.

DFT calculation details. We performed density functional theory calculations and ab initio molecular dynamics (AIMD) simulations using the Vienna Ab initio Simulation Package (VASP)28-30. The exchange-correlation Perdew–Burke–Ernzerhof functional and the ion–electron interaction as described by the plane-wave method were used.31,32 A plane-wave basis set with an energy cut-off of 400 eV was used with a Monkhorst-Pack k-point mesh of 13 × 13 × 1 for the geometry optimisation and the Γ point for the AIMD. The 4 × 4 silicene/Ag(111) system was modelled using the details published previously.33 To model adsorption of oxygen in this system, we initially placed oxygen atoms in top sites above the Si atoms at 1/2 ML coverage. A geometry optimisation was performed using medium precision, followed by high precision. During the optimisation the bottom 2 layers of Ag atoms were kept fixed, while all other atoms were allowed to relax until the total energy converged to <10⁻⁶ eV, and the Hellmann–Feynman force on each of the atoms was allowed to relax to <0.05 eV Å⁻¹. An ab initio molecular dynamics simulation of 7 ps, using a time step of 1 fs, followed by a subsequent partial geometry optimisation, showed that the Si layer becomes disordered and starts to delaminate from the Ag surface to form a silicon oxide type structure.

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**Author contributions**

X.X., J.Z. and Y.D. did the sample preparations and STM characterizations. N.Z., C.L., T.L. and J.W. did ARPES and XPS measurements. M.S. and T.M. performed DFT calculations. X.W., S.X.D. and H.F. helped with data analysis. X.X., J.Z. and Y.D. wrote the paper. X.X. and J.Z. contribute equally to this work.

**Additional information**

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