Supporting Information

Tuning the Band Gap in Silicene by Oxidation

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SI 1. Sample preparation and Characterizations

Sample Preparation

Silicene samples were grown on a Ag(111) substrate by sublimating Si from a 4×15 mm^2 piece of silicon wafer heated by a direct current at 1150°C. Clean Ag(111) substrate was prepared by an argon ion sputtering for 40 minutes with subsequent annealing at 820 K for 90 minutes. The annealing of the samples was repeated for several cycles in a preparation chamber of the STM system. The deposition of Si was performed at a flux rate of 0.08 monolayer per minute (ML/min) with varying substrate temperatures as follows: 450 K, 500 K, and 550 K to form $\sqrt{13}\times\sqrt{13}$, 4×4 and $2\sqrt{3}\times2\sqrt{3}$ phases, respectively. The number of silicene layers on Ag(111) substrate was controlled by adjusting deposition time. An *in-situ* oxidation process was performed to obtain oxidized silicene samples in STM preparation chamber. During oxidation, high-purity oxygen gas was introduced into the STM preparation chamber via ultra-high vacuum (UHV, $< 5\times10^{-11}$ torr) by a leak valve. Silicene samples were then oxidized under O_2 with 10 L (10 Langmuir, 1×10^{-6} torr for 10 sec), 60 L (1×10^{-6} torr for 1 min) and 600 L (1×10^{-6} torr for 10 min) at room temperature.

Characterizations

All samples in this work were characterized using a low-temperature scanning tunneling microscopy/scanning near-field optical microscopy system (LT-STM/SNOM) equipped with a preparation chamber (USM1500/SNOM1400, Unisoku Co., Japan). The STM as well as Raman spectroscopy measurements were carried in ultra-high vacuum (UHV, <8× 10-11 torr) at 77 K with Pt/Ir tips. In order to achieve maximum quality images and best dI/dV signal, the tips were firstly annealed by an electron-beam heating in the preparation chamber, which allowed re-crystallization of tip apex. Then, the tips were further sharpened and calibrated on a clean Ag(111) surface. STM topography images were obtained under a constant current mode with an active distance feedback loop. In-situ Raman spectra were gathered for silicene and silicene oxides with a laser wavelength of 532 nm^{-1}.The laser was focused on the sample by an incident lens driven by a piezomotor, as shown in **Figure S1**. Before each experiment, Raman system was calibrated on Si(111) standard sample. Extreme care was taken in order to avoid any sample damage or laser induced heating during Raman measurement. Such conditions were successfully achieved, which is evidenced by the fact that the surface structures of samples were not changed before, during, or after Raman measurements. The incident power during Raman measurements was varied between ~5 and ~0.5 mW. No significant spectral change, expect Raman signal intensity, was observed in this range.

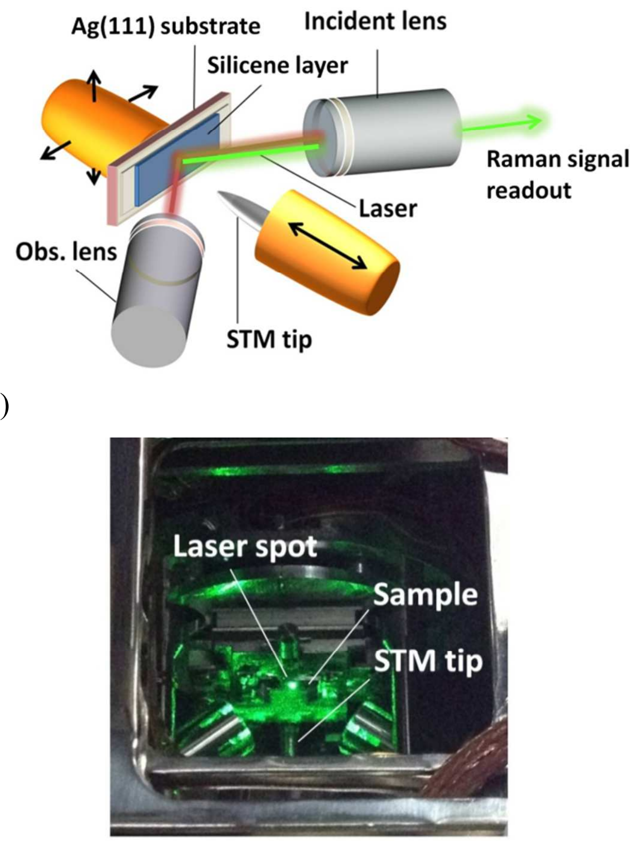

Figure S1: a, Schematic diagram of the low temperature STM system equipped with Raman attachment used in this study. The incident laser is introduced by an incident lens. The laser can be focused by the incident lens and optical image can be collected through the observation lens (indicated as Obs. lens in diagram). The Raman signal is reflected back and is collected by spectrometer which is attached to the incident lens. **b,** Actual image of the Raman measurement setup in the STM UHV chamber.

SI 2. Oxidation sites on silicene in different phases.

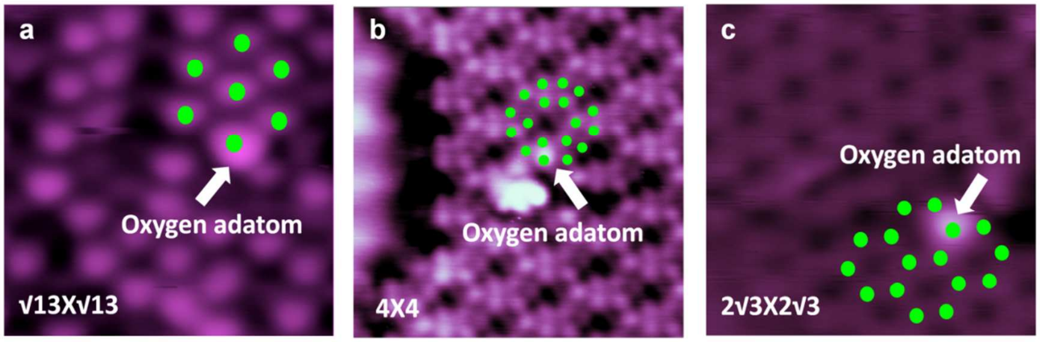

Figure S2. STM images of oxygen adatoms on silicene in different phases, (a) √13×√13, (b) 4×4 and (c) 2√3×2√3, on Ag(111) substrate. The bright protrusions are attributed to oxygen adatoms in each STM image. The green spots correspond to top-layer Si atoms in silicene. It indicates that oxygen adatoms prefer to reside at the top-layer silicon atoms in buckled silicene at initial oxidization stage.

SI 3. Oxidation of √13×√13 and 4×4 silicene structures.

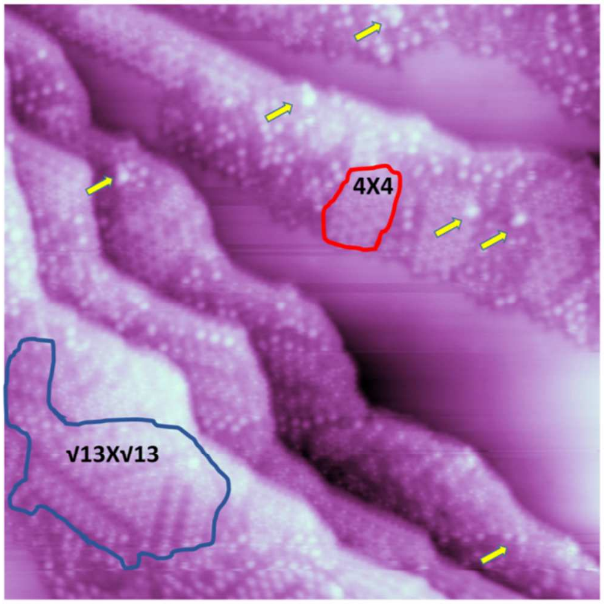

Figure S3. STM image of the √13×√13 and 4×4 mix-structured oxidized silicene layers on Ag(111). The coverage of silicene is 0.6 ML, specifically designed to study different roles of the edge and the surface during oxidation. Typical √13×√13 and 4×4 areas are circled in blue and red. The oxygen adatoms are marked by yellow arrows. All oxygen adatoms prefer to reside on the surface instead of the edge, which indicates that energy barrier for absorption of oxygen adatoms on surface is lower than the edge. (Sample was exposed to 10 L of O_2 before STM measurement. Scanning area 26×26 nm^2, V_{bias}= -0.15 V, I= 5 nA.)

Our measurements revealed that silicene monolayers with different structures show different oxidation behaviours. It was found that for all three structures the initial stage of oxidation always begins in the top-layer (TL) silicon atoms in buckled silicene monolayer, namely, √13×√13, 4×4 and 2√3×2√3. This would indicate that the energy required for the absorption of oxygen adatoms might be lower for TL silicon atoms as compared to the bottom-layer (BL) silicon. It is interesting that oxygen adatoms prefer to reside on the surface of silicene rather than the edge, which is totally different from graphene, as shown in **Figure S3** and **Figure S4**. This can be explained from the hybridization point of view. In the case of carbon in graphene, sp^2

hybridization is more energetically stable for honeycomb structures, however, sp^3 is energetically favoured form for silicon in the silicene. As a result, dangling bonds are expected on silicene surface as well as at edge. Once consideration of the interaction between silicon and silver atoms is taken into account, the edged Si atoms are likely to have stronger bonding with Ag than Si atoms at the surface. The energy barrier for absorption of oxygen adatoms, therefore, is lower at the surface. However, further investigations, such as Kelvin probe force microscopy are required in order to fully understand oxygen bonding features on silicene. These experiments will be carried out in the near future.

SI 4. Oxidation of 2√3×2√3 silicene structures

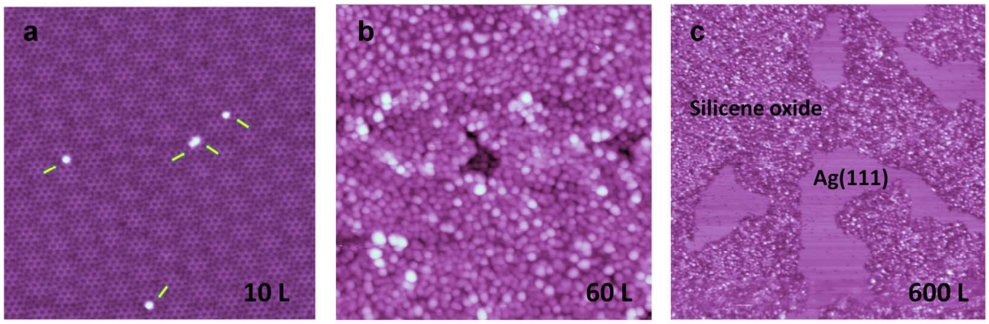

Figure S4. STM images of 2√3×2√3 silicene structures after oxidation under (a) 10 L O_2, (b) 60 L O_2 and (c) 600 L O_2. Shrinkage of silicene oxide results in the exposure of bare Ag(111) surface (c). (V_{bias}= 0.8 V, I= 2 nA)

SI 5. Raman spectra of silicene and silicene oxides.

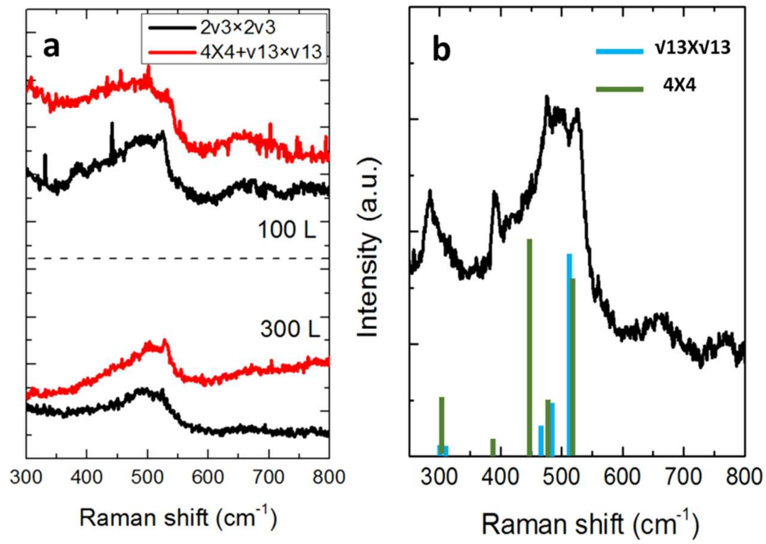

Figure S5. (a) Raman spectra of silicene oxidized under 100 L and 300 L O_2. (b) Raman spectra of mixed √13×√13/4×4 silicene. The Raman peaks are assigned according to the theoretical simulation results reported in previous work.

SI 6. STS measurements on oxidized silicene layers

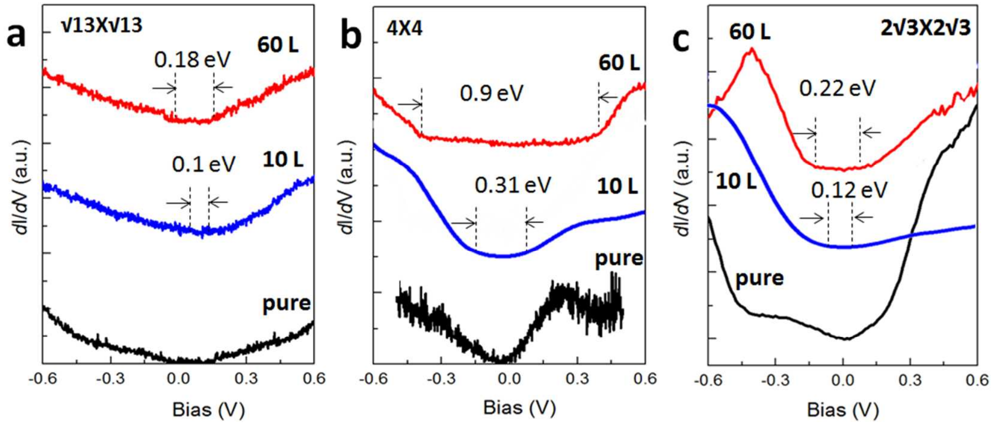

Figure S6. STS *d*I/*d*V curves measured on silicene layers oxidized under various oxygen doses. Band gap can be tuned by oxygen doses in oxidation for √13×√13, 4×4 and 2√3×2√3.

SI 7. Density of states of silicene layers with oxygen adatoms.

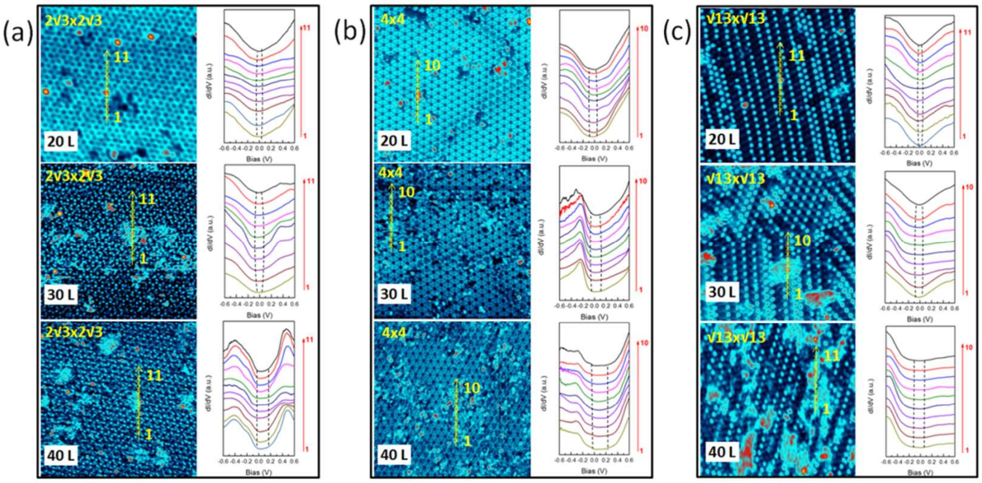

Figure S7. STM images and spatial STS *d*I/*d*V curves measured on (a) 2√3×2√3, (b) 4×4, and (c) √13×√13 silicene layers oxidized under various oxygen doses from 20 L to 40 L. Tunneling spectra (*d*I/*d*V curves) were obtained along a line denoted by the arrows in the corresponding STM topographic images on the right. The dashed lines in each STS result illustrate the value of band gap. STM images were obtained at $V_{\text{bias}} = -0.8$ V, $I = 0.6$ nA. Scanning area is 24×24 nm^2. The oxygen adatoms appear as bright protrusions on the silicene layers.

SI 8. Density of states of silicene layers with oxygen adatoms.

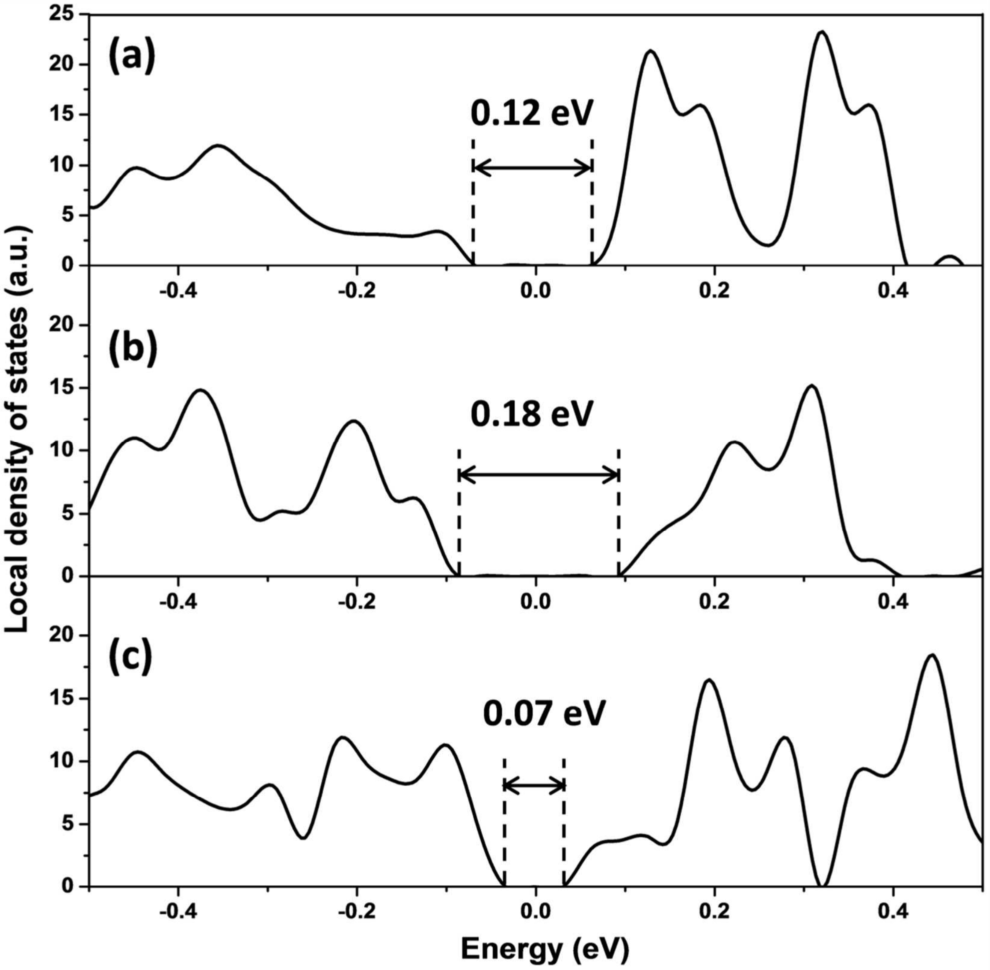

Figure S8. DFT calculated density of states of (a) √13×√13, (b) 4×4 and (c) 2√3×2√3 silicene layers with oxygen adatoms (oxygen dose is 10 L).