# Multilayer Silicene: The Bottom-Up Approach for a Weakly Relaxed Si(111) with Dirac Surface States

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## Supplementary Information

### Definition of cohesive and binding energies

For free-standing silicon sheets, the cohesive energy $E_c$ and binding energy $E_{b1}$ are defined as $E_c = -E_N/N_{Si} + \mu_{Si}$ and $E_{b1} = (E_{(N-1)} + E_1 - E_N)/ n_{Si}$, respectively. While they are $E_c = (E_{Ag} - E_{N/Ag})/ N_{Si} + \mu_{Si}$ and $E_{b1} = (E_{(N-1)/Ag} + E_1 - E_{N/Ag})/n_{Si}$ for multilayer silicene on silver substrates. A second binding energy $E_{b2}$, $E_{b2} = (E_N + E_{Ag} - E_{N/Ag})/ n_{Si}$, is used to describe the interaction between silicon films and silver substrate. Here $E_{Ag}$, $E_N$, $E_{N/Ag}$ are the total energy of clean Ag substrate, N-layer Si(111), N-layer Si(111) on Ag, respectively. $N_{Si}$ is the total number of silicon atoms in the system, and $n_{Si}$ is the number of Si atoms in an atomic layer. $\mu_{Si}$ is the chemical potential of Si adopting the value of total energy for a single Si atom in vacuum.

**Table S1.** Buckling distances ($\Delta Z$) and mean square displacements (MSD) in atomic structures for monolayer and five-layer √3×√3 silicene films on Ag(111) surfaces, as well as for √3×√3 Si-Ag alloy on Si(111) and Ag(111).

| | 1L-Si/Ag | 5L-Si/Ag | SiAg-√3/Ag | SiAg-√3/4L-Si(111)/Ag |
|---|---|---|---|---|
| $\Delta Z$ (Å) | 1.0 | 1.1 | 1.2 | 0.8 |
| MSD (Å$^2$) | 0.006 | | 0.05 | |

Table S2. Total transfer charge from Si to Ag (unit: $e^-$):

| 1L-Si/Ag | 2L-Si/Ag | 3L-Si/Ag | 4L-Si/Ag | 5L-Si/Ag |
|---|---|---|---|---|
| 0.83 | 0.56 | 0.54 | 0.48 | 0.46 |

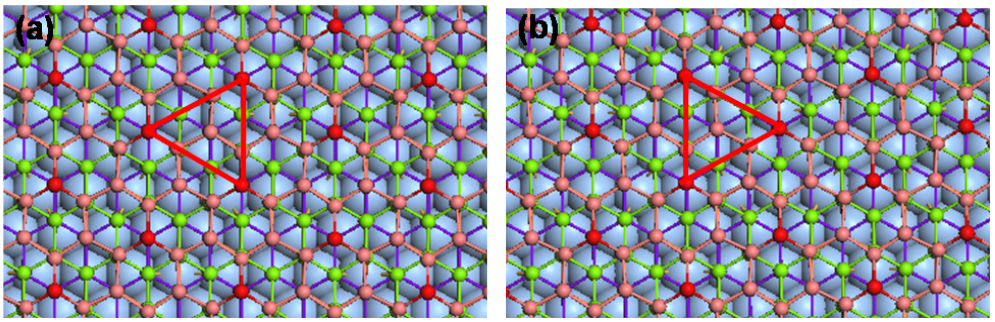


**Figure S1.** Top views of two mirror-symmetric √3 phases for the 5-layer Si films on Ag(111). Small and big spheres denote the Si and Ag atoms, respectively. The red triangles denote the orientation of the buckled Si patterns on the topmost layer.

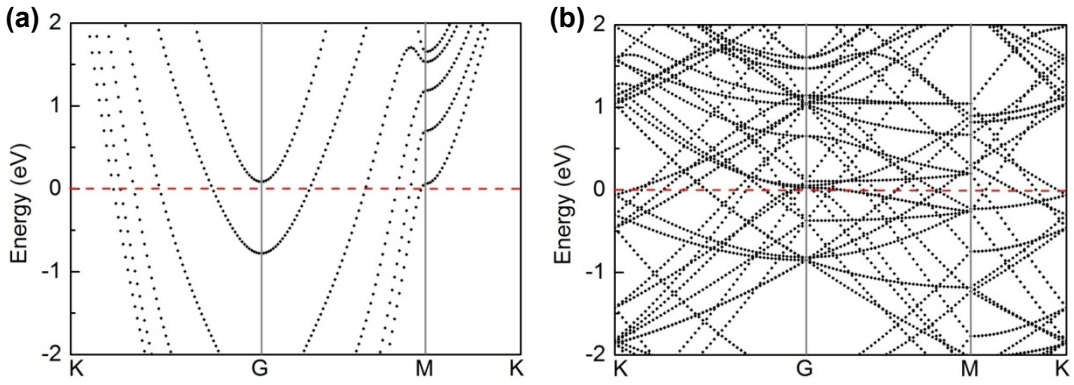


**Figure S2.** Band structures of bare 5-layer Ag(111) in the (a) 1×1 and (b) 4×4 surface supercell.

**(a)** **(b)**

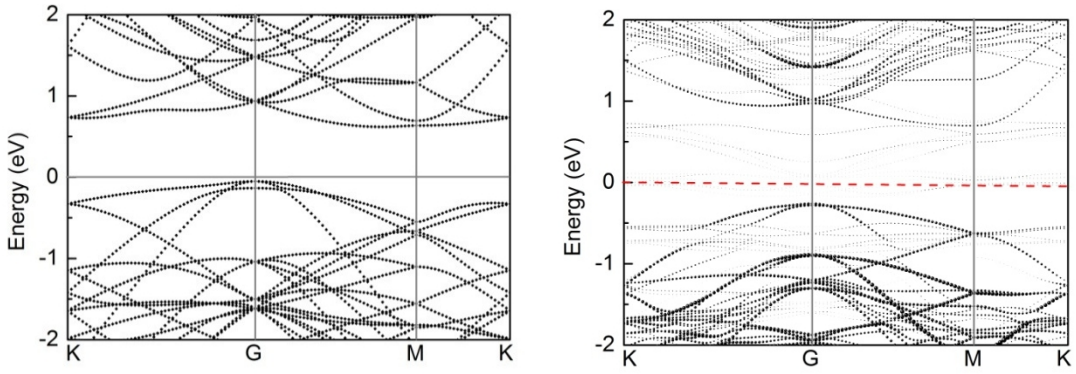


**Figure S3.** (a) Band structure of infinite layer Si(111) in a 3×3 surface supercell, and (b) the projected band structures on the third (middle) Si atomic layer of free- standing 5-layer Si(111) film.

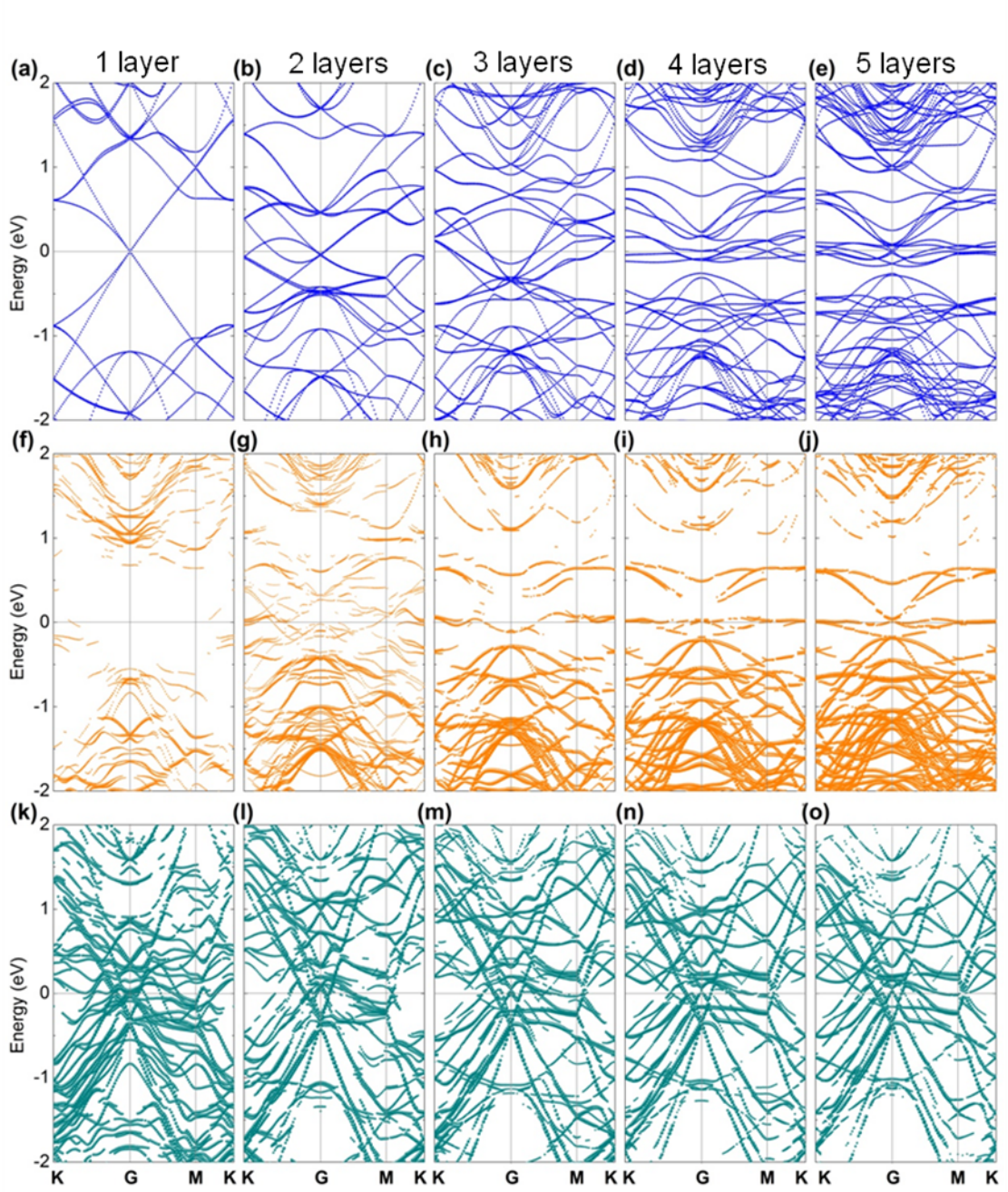


**Figure S4.** Band structures for (a-e) free-standing and (f-o) epitaxial Si films. Panels from left to right are for films with a thickness of 1 to 5 layers. Orange and cyan dots denote projected bands onto all Si (f-j) and Ag atoms (k-o), respectively. The size of dots corresponds to the weight of contribution.

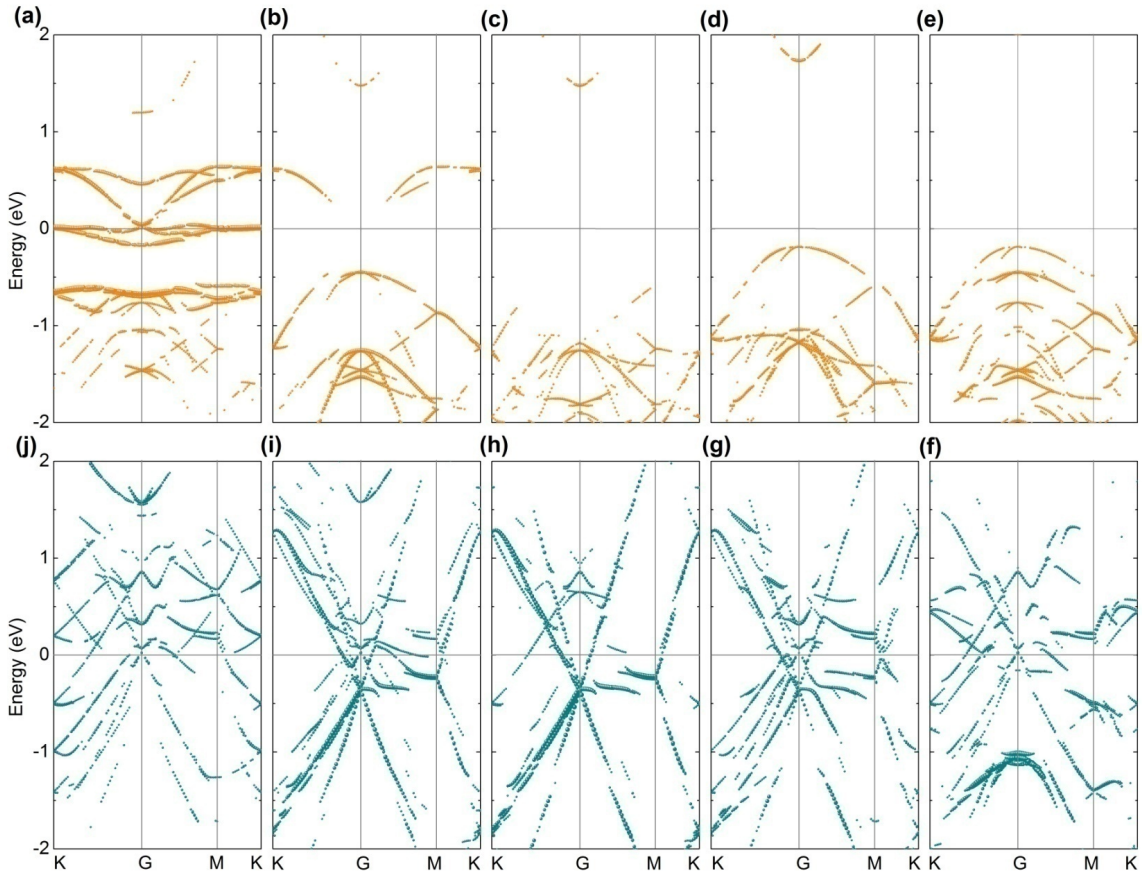


**Figure S5**. Projected band structures onto each atomic layer for 5-layer Si on the 5-layer Ag(111). From (a) to (e) are bands projected onto the topmost, 2nd, 3rd, 4th, and bottom Si layer. From (f) to (j) are bands projected onto the first to the bottom Ag layer counting from the Si/Ag interface.

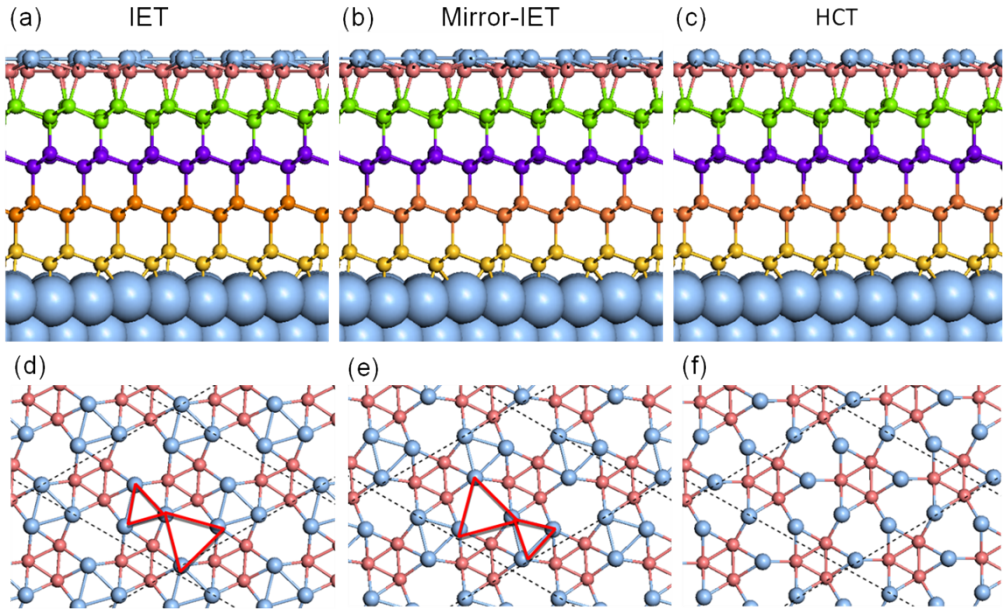


**Figure S6.** (a-c) Side and (d-f) top views of IET (inequivalent triangles), Mirror-IET (mirror-symmetrical phase for IET), as well as HCT (honeycomb-chained triangles) structures of Si(111)-√3×√3-Ag layer on Si(111)/Ag(111). The blue spheres denote Ag atoms, and the red, green, purple, orange, yellow spheres denote Si atoms in the 1$^{st}$, 2$^{nd}$, 3$^{rd}$, 4$^{th}$, 5$^{th}$ silicon layers, respectively. In the top views, only the top layer atoms are visible.

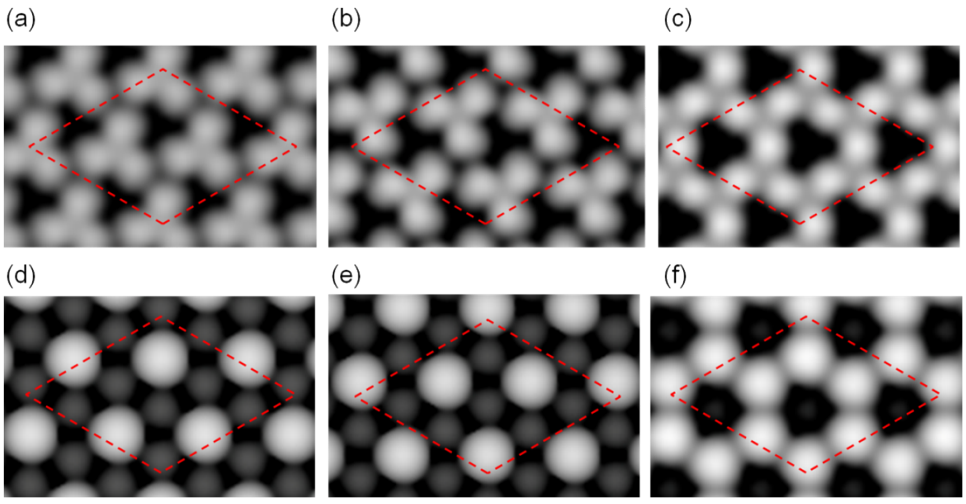


**Figure S7.** Simulated STM images of (a) IET, (b) mirror-IET, and (c) HCT structures (shown in Figure S6), as well as (d, e) low-temperature, and (f) high-temperature structures of √3×√3 five-layer silicene surface, using constant current mode based on calculated electronic densities within the energy range of [$E_F$-1eV, $E_F$].

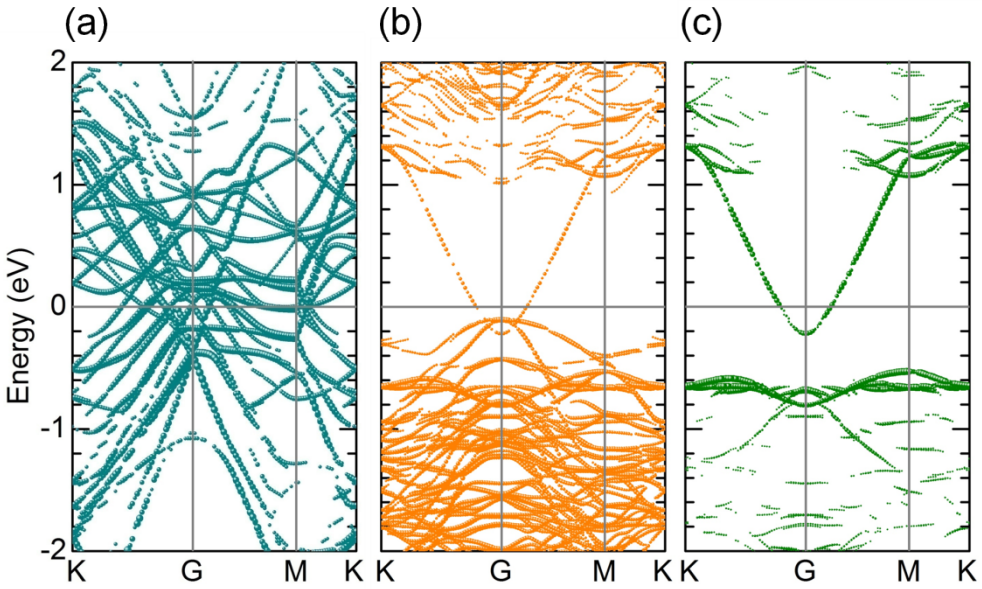


**Figure S8.** Projected band structures onto (a) 5-layer Ag substrate, (b) top five atomic layers, and (c) topmost surface layer for the IET structure in Fig. S6. The effective electron mass fitted to the parabola curve in (c) is 0.09 $m_e$ ($m_e$, mass of free electrons).

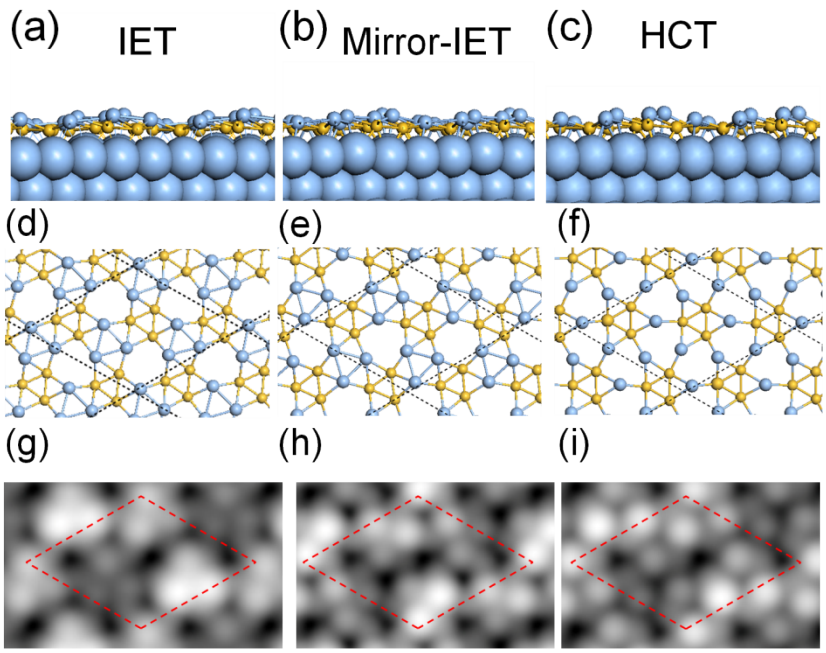


**Figure S9.** (a-c) Side and (d-f) top views of IET, mirror-IET, and HCT structures of √3×√3 Si-Ag alloy single-layer on Ag(111) surface. (g-i) Simulated STM images of the three structures within the energy range of [$E_F$-1eV, $E_F$].

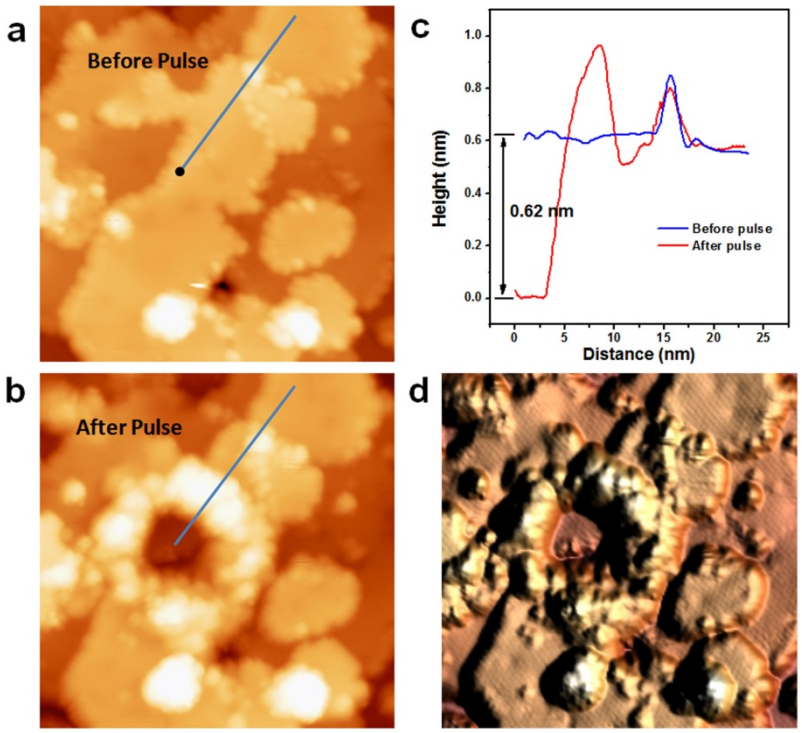


**Figure S10.** (a) and (b) The STM images of same area ($V_{tip}$ = 1 V, 40×40 $nm^2$) taken before and after applying a series of bias pulses (5V, 50ms) at the position marked by the black dot in (a). (c) The line profiles along the blue lines in (a) and (b) respectively, indicating that two atomic layers have been removed inside the pit. (d) Three-dimensional version of (b) to emphasize the atomic structures of top layer inside and outside the pit.