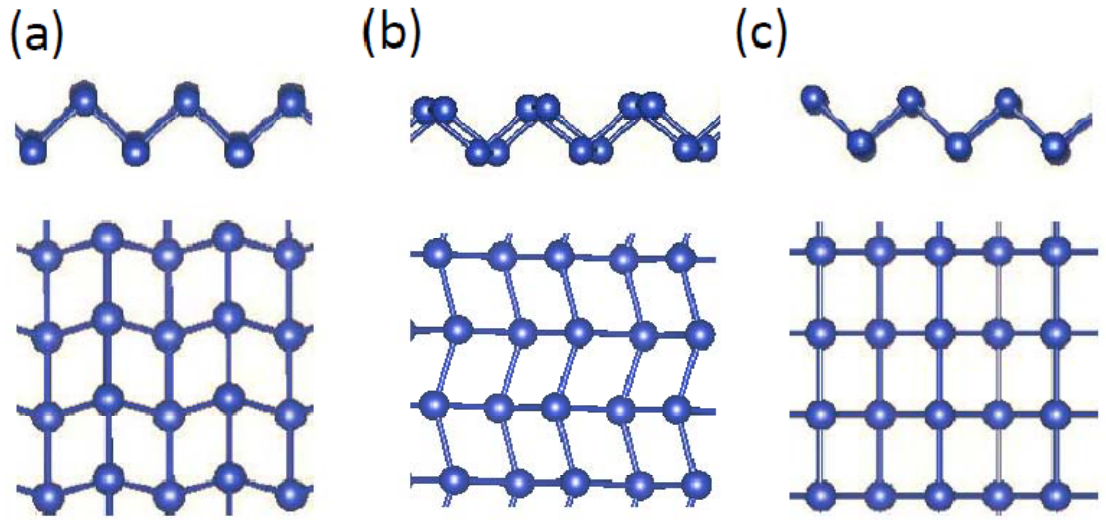

Figure S1. Side (upper panels) and top (bottom panels) views of the stable phases of newly obtained freestanding monolayer silicene, which have larger cohesive energy (E_c) than the well-known low-buckled honeycomb silicene phase (E_c=4.75 eV/Si). (a) silicene phase with E_c=4.77 eV/Si; (b) silicene phase with E_c=4.78 eV/Si; (c) silicene phase with E_c=4.77 eV/Si. From the calculated phonon dispersions (not shown), these new silicene phases are not dynamically stable.

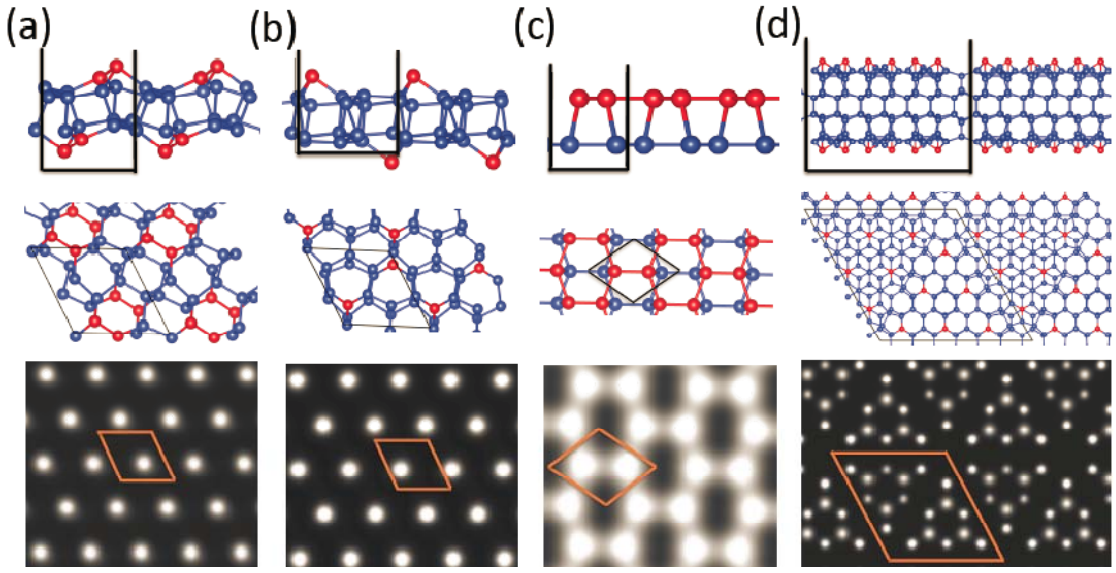

Figure S2. Side (upper panels) and top (middle panels) views of stable phases of freestanding multilayer silicene and corresponding occupied STM images (bottom panels). (a) P-1-2x2 bilayer silicene, (b) C12/m1-2x2 bilayer silicene, (c) Cmme-1x1 bilayer silicene, (d) 7x7 quadlayer silicene with DAS structure. The phonon dispersions of silicene phases in (a), (b) and (c) can be found in *Phys. Rev. B 91, 201405 (2015)*, which shows that the three silicene phases are dynamically stable. The lateral unit cells are indicated by the solid lines.

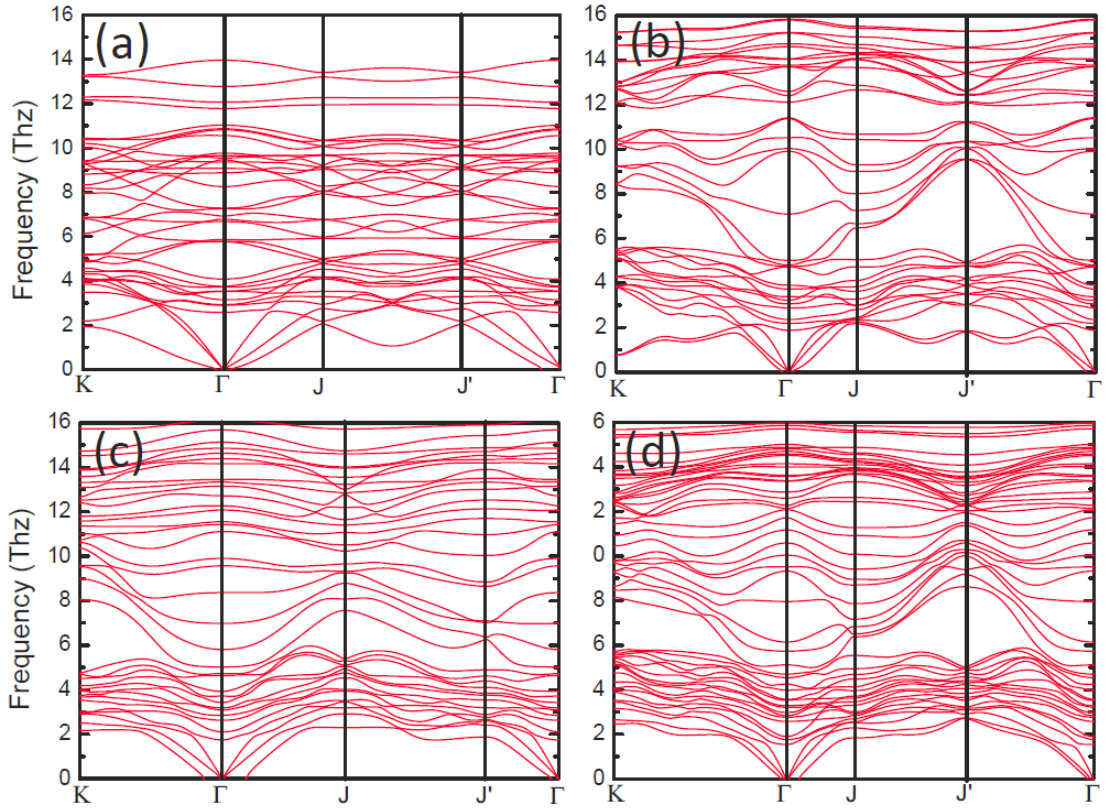

Figure S3. Phonon dispersions of newly obtained multilayer silicene phases in Fig. 1. (a) C12/m1-$\sqrt{2}$ x $\sqrt{2}$ bilayer silicene, (b) P121/m1-2×1 and (c) P1-2×1 trilayer silicene, (d) P1m1-2×1 quadlayer silicene. From the phonon dispersions, these silicene phases are dynamically stable.

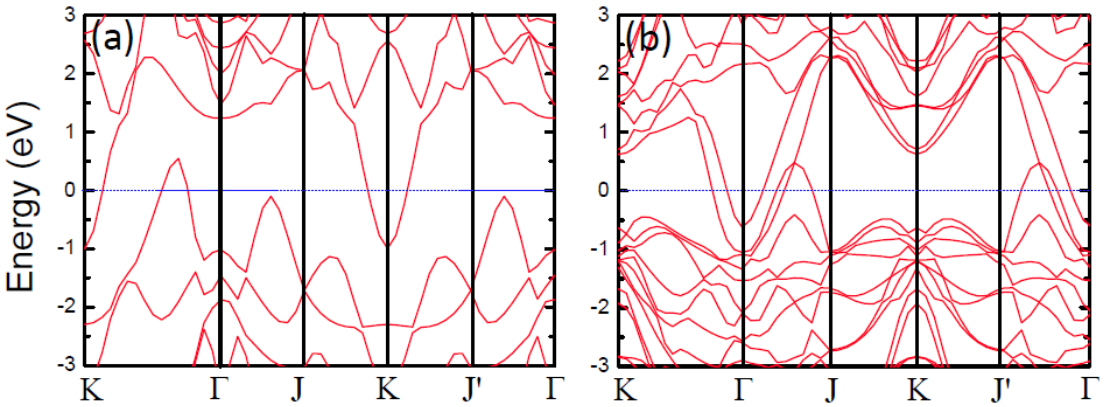

Figure S4. Calculated energy bands of metallic silicene phases. (a) Cmme-1x1 bilayer silicene; (b) C12/m1-$\sqrt{2}$ x $\sqrt{2}$ bilayer silicene. The Fermi energy is set to be 0.

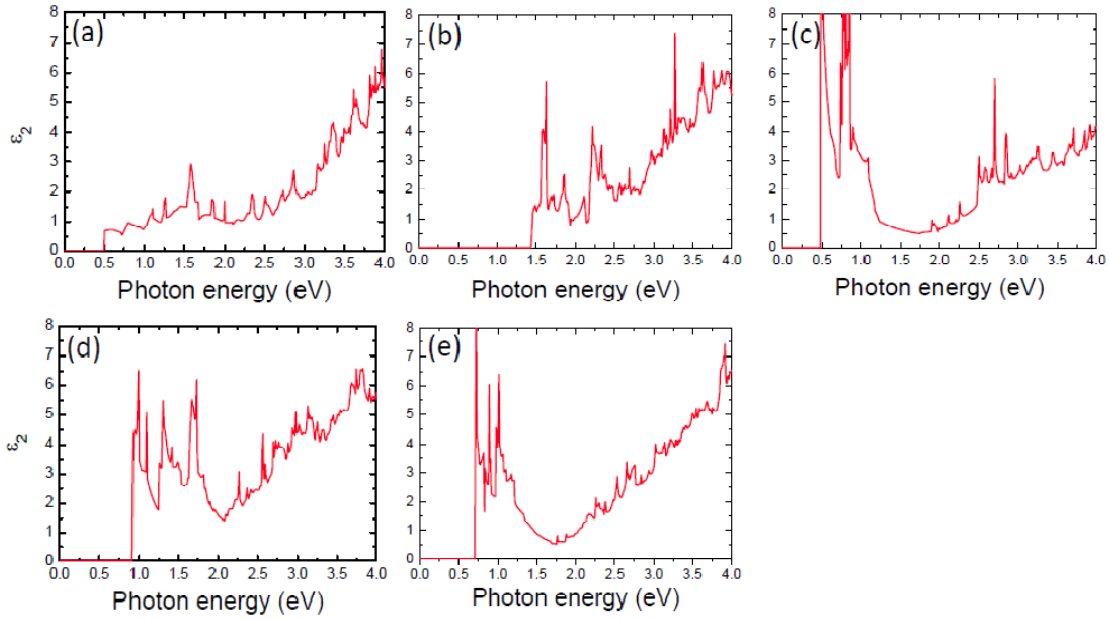

Figure S5. Calculated imaginary part of dielectric functions (ε_2) of semiconductor multilayer silicene. (a) C12/m1-2×2 bilayer silicene, (b) P-1-2 × 2 bilayer silicene, (c) P121/m1-2×1 trilayer silicene, (d) P1-2 × 1 trilayer silicene, (e) P1m1-2 × 1 quadlayer silicene.

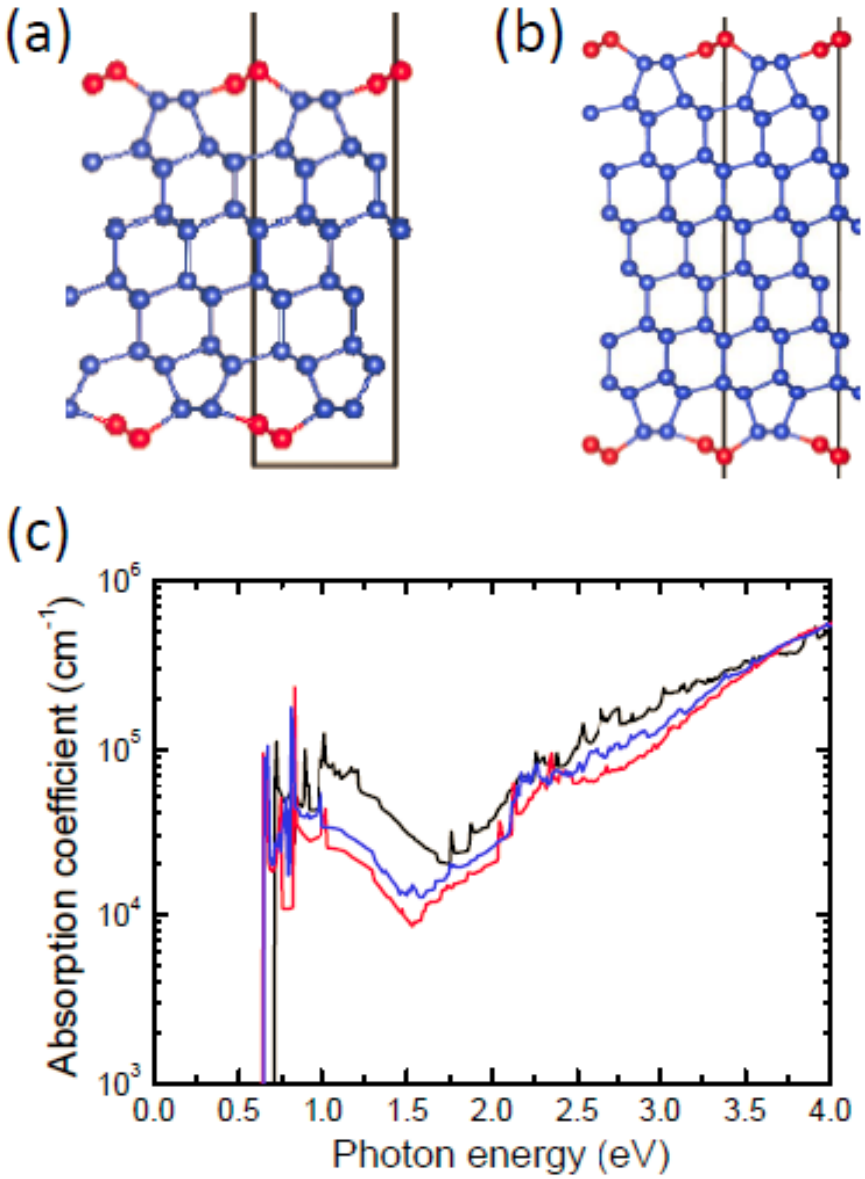

Figure S6. Geometries and optical absorption coefficients of 2x1 multilayer silicene with π-bonded chain surfaces. (a) and (b) Geometries of 2x1 multilayer silicene with thickness being 6 and 8 Si layers, respectively. (c) Optical absorption coefficients of the 6- and 8-layered 2x1 silicene with compare of the 4-layered 2x1 silicene. The highly protruded Si atoms at the surfaces are depicted by the red balls and the remaining Si atoms are depicted by the blue balls. The black, blue and red lines correspond to the silicene with thickness of 4, 6 and 8 Si layers, respectively.