Supporting Information

Electronic Structure of Quasi-free-standing Germanene on

Monolayer MX (M=Ga, In; X=S, Se, Te)

Zeyuan Ni[1], Emi Minamitani[1], Yasunobu Ando[1], Watanabe Satoshi[1,*]

[1]Department of Materials Engineering, The University of Tokyo, Tokyo 113-8656, Japan

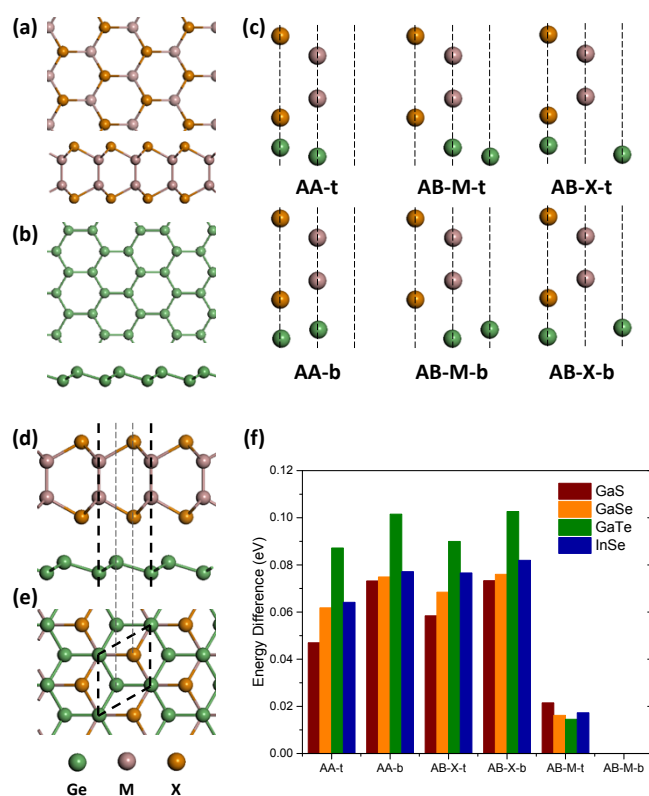*Corresponding authors: zeyuan_ni@ cello.t.u-tokyo.ac.jp; watanabe@cello.t.u-tokyo.ac.jp

Figure S0 (Figure 1, provided here for the convenience of reference): Top and side views of free standing ML (a) MX and (b) germanene. (c) All the six high symmetric stacking configurations of germanene on MX. (d) Side and (e) top views of 1 × 1 stacked ML germanene and MX with the most preferable stacking. Thick dashed lines denote the lattice, and thin dashed lines denote the high symmetric positions in hexagonal cells. M = Ga, In; X = S, Se, Te. (f) Energy difference between AB-M-b configuration and the other configurations.
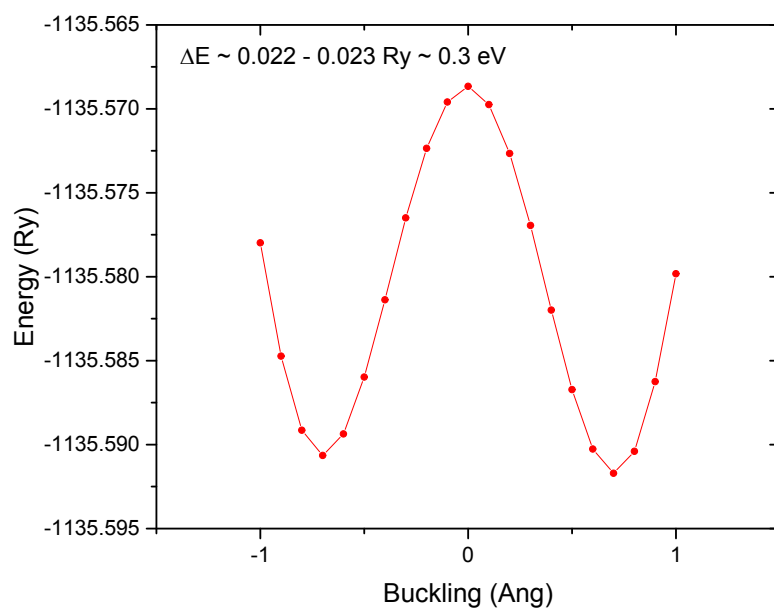
Figure S1: Total energy of germanene on GaTe with different buckling height. The whole system is geometrically optimized while germanene is fixed. The left and right minimums correspond to AB-M-t and AB-M-b configurations, respectively.
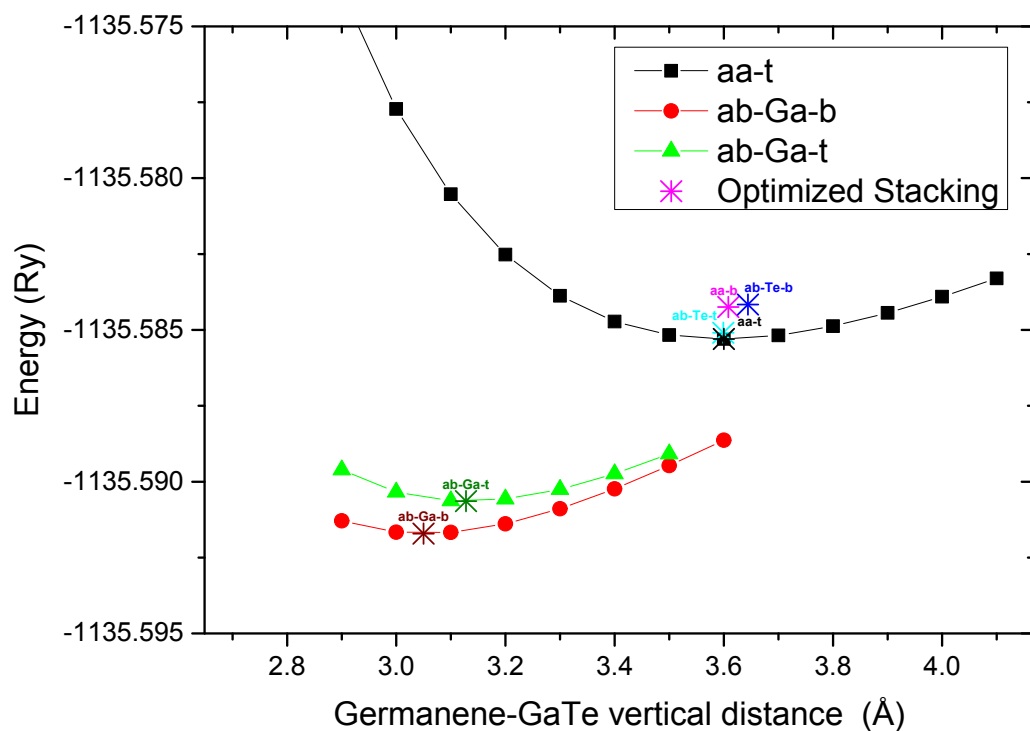
Figure S2: Total energy of GaTe-germanene system with all 6 kinds of stacking. Stars denote the energy given by geometry optimization. Lines denote the energy change by changing the vertical distance between optimized and fixed germanene and GaTe.
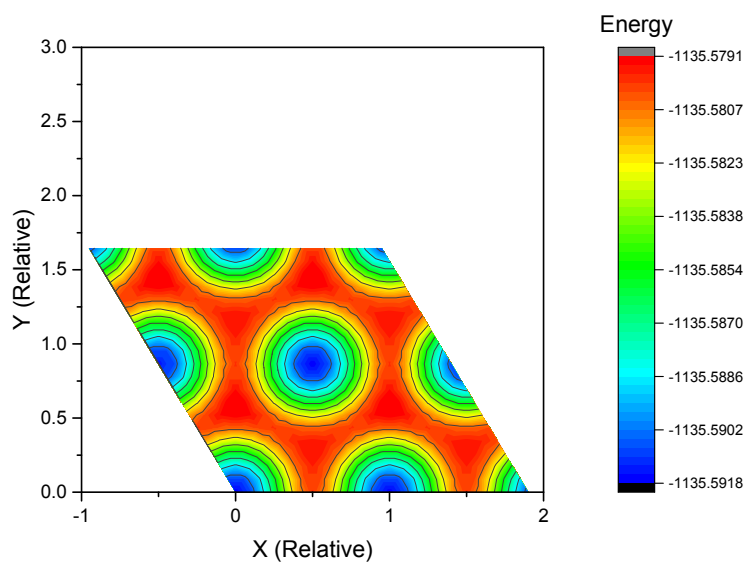

Figure S3: Energy map of germanene on GaTe with different lateral relative position while keeping the vertical distance between germanene and GaTe. The configuration at X=Y=0 is the AB-M-b
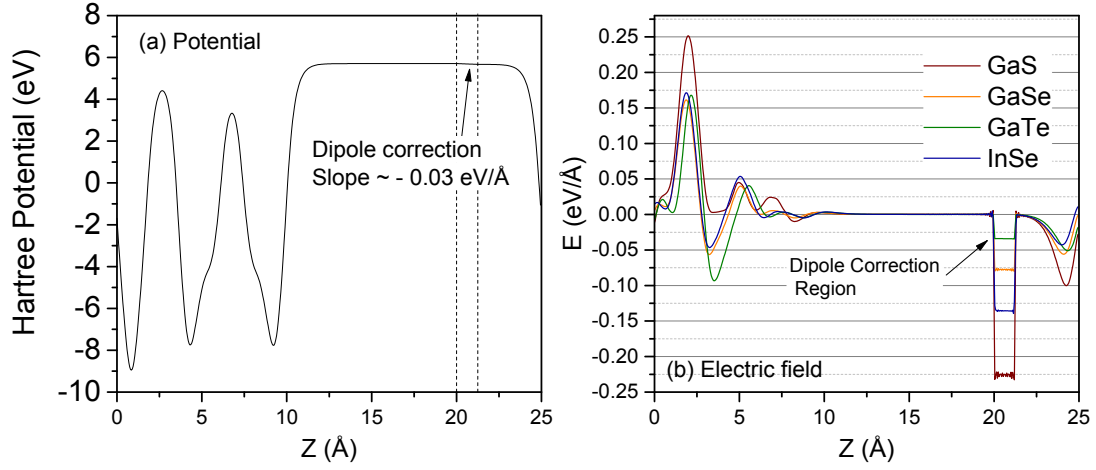
configuration.

Figure S4: (a) Potential diagram averaged in the XY-plain along Z-direction of the germanene-GaTe system. (b) Electric field diagram of averaged in the XY-plain along Z-direction of the germanene-MX system. The electric field is the differential of the differential potential, i.e.

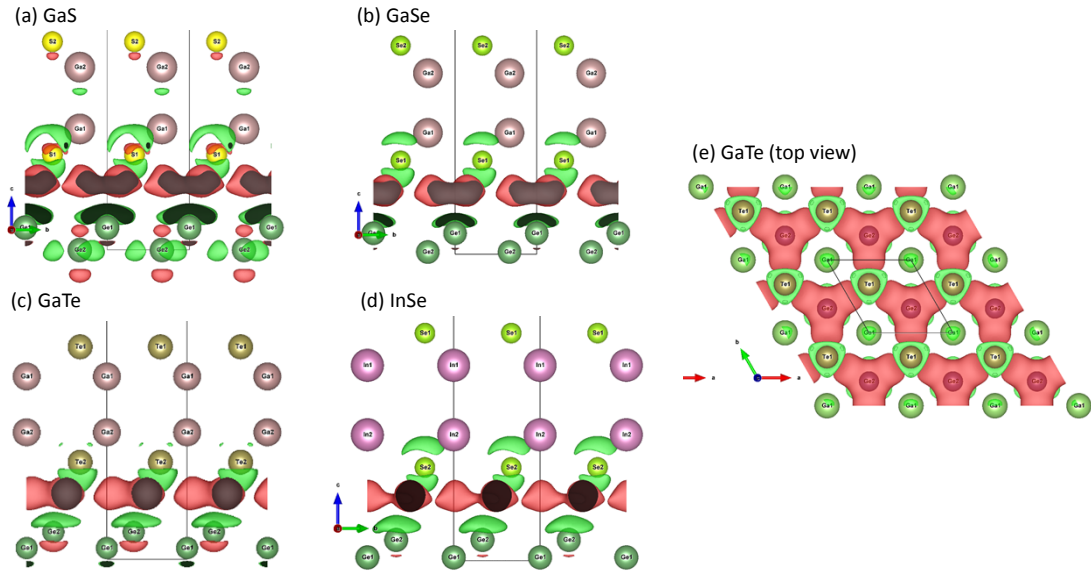$$\frac{d(P_{germanene-MX} - P_{germanene} - P_{MX})}{dZ}.$$

Figure S5: Differential charge density of germanene-MX systems. Ge atoms are in the bottom part of each figure and are colored in dark green. The isosurface is chosen as 0.0025. Red and green colors indicate positive and negative values, respectively.
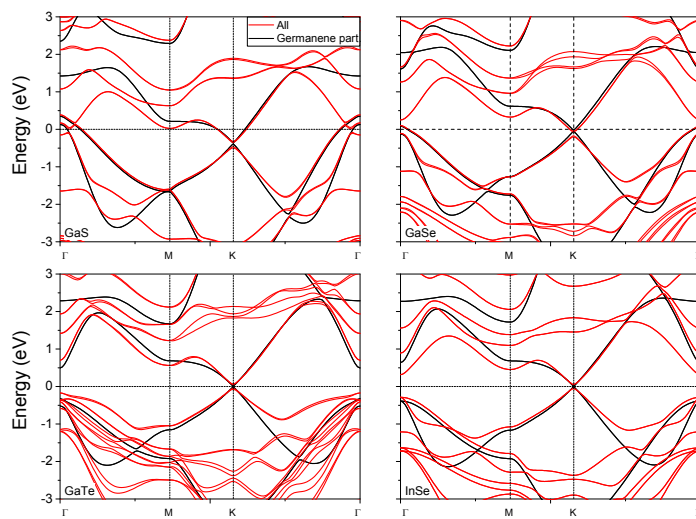
Figure S6: Band structure of Germanene-MX systems and the germanene parts only. The band structure of the corresponding germanene part is calculated by simply removing the MX part to see the effect of deformation on germanene.
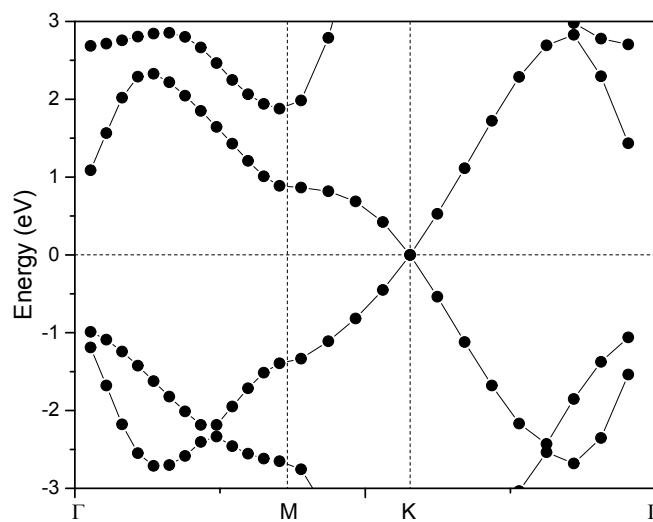

Figure S7: Band structure of free-standing germanene calculated using the HSE functional. It is in accordance with the HSE band structure given by Matthes *et. al.* (*J. Phys.: Condens. Matter* 2013, 25, 395305).
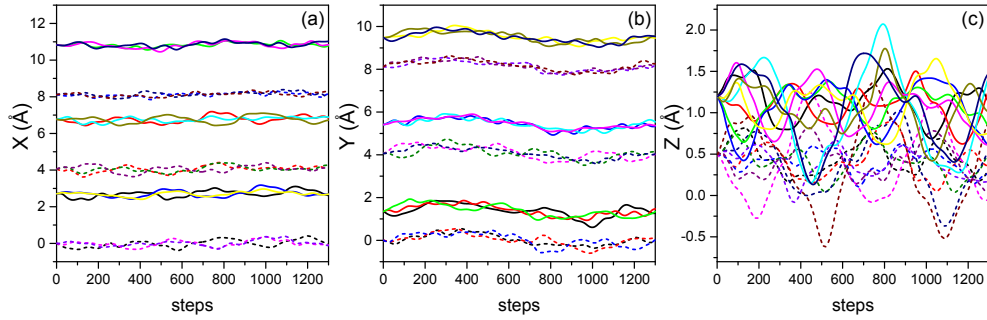
Figure S8: (a) X, (b) Y, and (c) Z positions of all Ge atoms at every step of molecular dynamics simulation of germanene on GaTe at 500K. A 3 x 3 supercell is used in the simulation, so there are 18 Ge atoms in total. Dashed lines stands for those Ge atoms that start at a lower Z position ("bottom" Ge), while solid lines for those at a higher Z position ("top" Ge). One step is 1.5 fs. Note that the X and Y positions of Ge atoms oscillates around their initial positions, indicating a rather stable configuration. On the other hand, the Z position of Ge atoms changes more greatly and sometimes local flipping of "top" and "bottom" Ge happens. Although the non-local flipping (flipping of all "top" and "bottom" Ge) is proved to have large energy barrier of 0.3 eV previously, local flipping engages less atoms and experiences much lowered energy barrier, making it possible to happen. The molecular dynamics simulation is performed by VASP in a 3 × 3 supercell under 500 K using the Nosé–Hoover canonic thermostat.
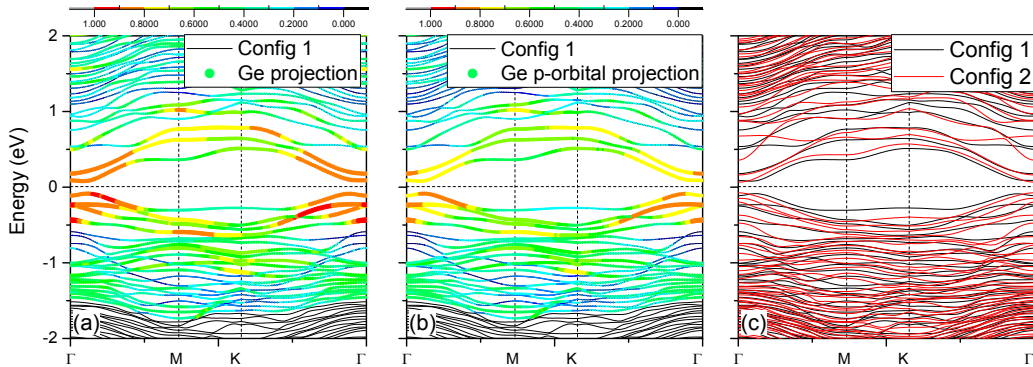

Figure S9: Band structure of germanene on GaTe during molecular dynamics (MD). (a) & (b) Band structure of a random configuration during MD of germanene on GaTe with projection of (a) all orbitals and (b) only p-orbital of Ge. The size of the dots indicates the absolute projection value and the color indicates the percentage of the projection in total. (c) Band structure of two random configurations during MD. Note that the MD is done in a 3 x 3 supercell, and the K point of the primitive cell is folded to the Γ point in such a supercell. As we know, the Dirac cone of germanene is mainly contributed by the p-orbitals of Ge atoms. Since the bands near the Fermi energy and the Γ point in (b) are also mainly contributed by p-orbitals of Ge, we believe it is a deformed Dirac cone. In

addition, the MD is done at 500K, which should have overestimated the deformation of geometry and probably the band structure compared with the case at room temperature. Last but not least, it is too naïve using this MD result to interpret the electronic structure of germanene on MX at finite temperature. They are only two transient configurations with little representativeness of the overall property of germanene. Further study on the electron-phonon coupling of germanene on MX is required to provide such overall electronic structure at finite temperature, but it's beyond the scope of this work.
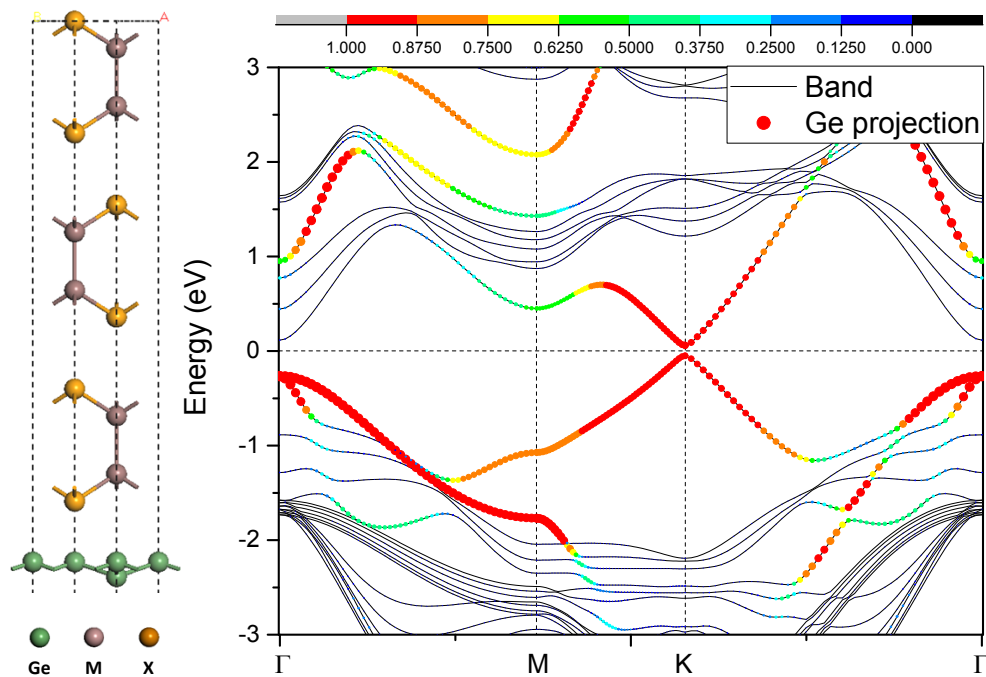

Figure S10: Geometry and band structure of germanene on 3-layer InSe. The size of the dots indicates the absolute value of Ge projection, and the color indicates the percentage of Ge projection in total. Germanene has similar band structure as when it is on ML InSe.