Electronic supplementary information:

Dissociative adsorption of guanine on Ge(100)

Young-Sang Youn,[*,a,b] *Do Hwan Kim,*[*,c] *Hye Jin Lee,*[d] *and Sehun Kim*[a]

1. Experimental and computational methods

A Ge(100) surface (n-type, Sb doped, R≈ 0.10 Ω) was cleaved to a size of 2 × 10 mm^2 to perform the STM experiments. The Ge(100) surface was cleaned by being subjected to several sputtering cycles using Ar^+ ions (1 keV, 20 min, 700 K). This was followed by annealing at 900 K for 10 min. The cleanliness of the Ge(100) surface was checked with STM. Guanine ($C_5H_5N_5O$, 98% purity) was purchased from Aldrich and purified through several sublimation and pumping cycles to remove all dissolved gases prior to dosing. To obtain the appropriate vapor pressure for dosing, the dosing line was heated during guanine deposition.

The STM observations were performed in an ultrahigh-vacuum (UHV) chamber equipped with an OMICRON VT-STM instrument. The base pressure was lower than 1.2×10^{-10} Torr. All the STM images were recorded with an electrochemically etched tungsten tip at a bias voltage, V_s, of −2.0 V and tunneling current, I_t, of 0.1 nA.

To investigate the adsorption configurations of guanine on the Ge(100) surface, we performed ab initio calculations using gradient-corrected density-functional theory (DFT–GGA); the Vienna ab initio simulation package (VASP) was employed for the purpose.[1] Plane waves with a cutoff energy of 400 eV were included to expand the wave functions, and the ions were represented by the project-augmented-wave (PAW) potentials and Grimme's DFT-D2 vdW, as provided by VASP.[2, 3] The slab

model of the guanine-adsorbed Ge(100) surface consisted of the adsorbed guanine molecules, six Ge atomic layers, and an H passivating layer. Each Ge atom of the bottom layer was passivated with two H atoms. We used a p(4×4) supercell with a c(4×2) surface symmetry. The topmost four layers of the slab and the adsorbed molecules were allowed to relax with respect to the calculated Hellmann-Feynman forces, and the two remaining Ge layers were kept frozen during structure optimization. The surface structure was considered to be in equilibrium when the Hellmann–Feynman force was less than 0.02 eV/Å. For the Brillouin-zone integration, we used a 2×2×1 grid in the Monkhorst-Pack special point scheme. In addition to using self-consistent Kohn–Sham eigenvalues and wave functions, the constant-current STM images were simulated with the Tersoff–Hamann scheme.[4, 5] The tunneling current I(r, ±V) is proportional to the energy-integrated local density of states:

$$I(\mathbf{r},\pm V) \propto \sum_{\mathbf{nk}} \int_{E_F}^{E_F \pm V} \left|\psi_{n\mathbf{k}}(\mathbf{r})\right|^2 \delta(E - E_{n\mathbf{k}})dE$$

where +V and –V are the sample bias voltages for the empty-state and filled-state measurements, respectively.

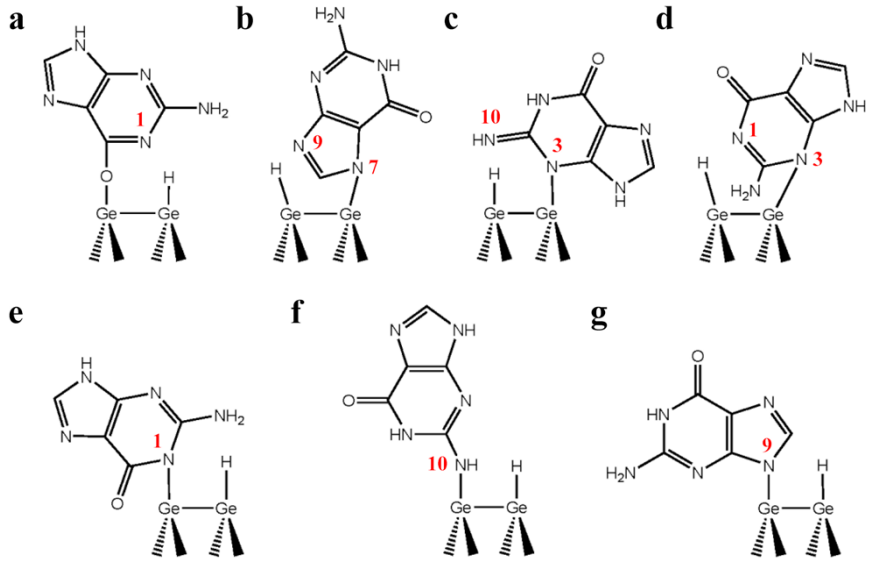

Figure S1. Schematics of the possible reaction pathways through N-H dissociation in guanine on Ge(100): (a) N(1)-H dissociation through an O dative bonded structure, (b) N(9)-H dissociation through a N(7) dative bonded structure, (c) N(10)-H dissociation through a N(3) dative bonded structure, (d) N(1)-H dissociation through a N(3) dative bonded structure, (e) N(1)-H dissociation structure, (f) N(10)-H dissociation structure, and (g) N(9)-H dissociation structure.

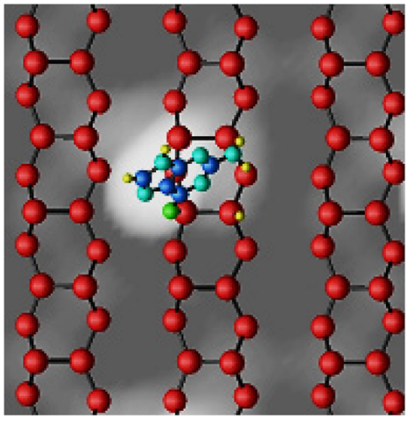

Figure S2. Theoretically simulated filled-state STM image for the N(1)-H dissociation through an O dative bonded structure. The blue, teal, green, yellow, and red balls represent carbon, nitrogen, oxygen, hydrogen, and germanium atoms, respectively.

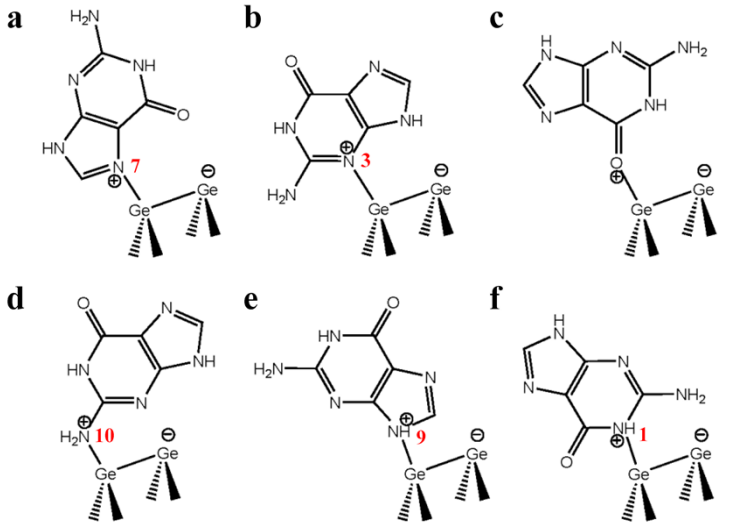

Figure S3. Schematic illustrations of the possible adsorption configurations through the dative bonding of guanine on Ge(100): (a) N(7) dative bonded structure, (b) N(3) dative bonded structure, (c) O dative bonded structure, (d) N(10) dative bonded structure, (e) N(9) dative bonded structure, and (f) N(1) dative bonded structure.

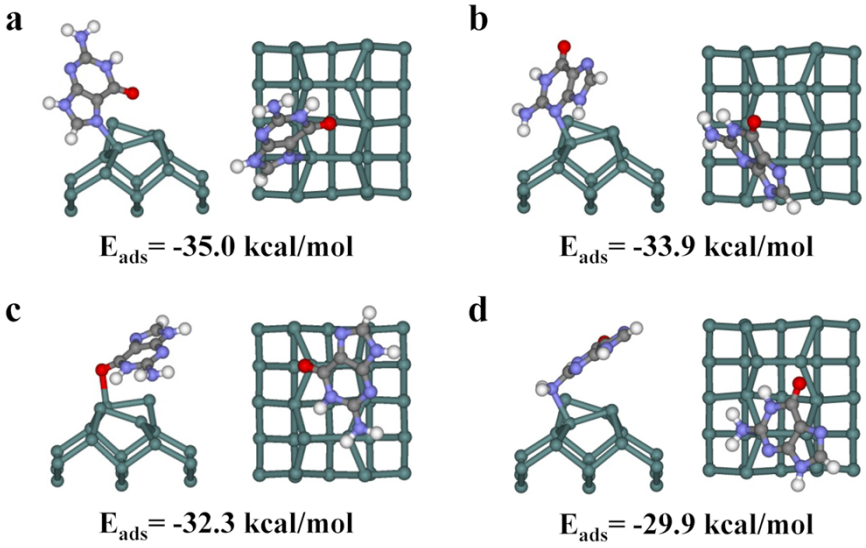

Figure S4. Optimized adsorption structures and the corresponding adsorption energies (E_{ads}) of (a) N(7) dative bonded structure, (b) N(3) dative bonded structure, (c) O dative bonded structure, and (d) N(10) dative bonded structure. The gray, blue, red, white, and teal balls represent carbon, nitrogen, oxygen, hydrogen, and germanium atoms, respectively.

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