Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic supplementary information

Two-dimensional silicene nucleation on a Ag(111) surface: structural evolution and the role of surface diffusion

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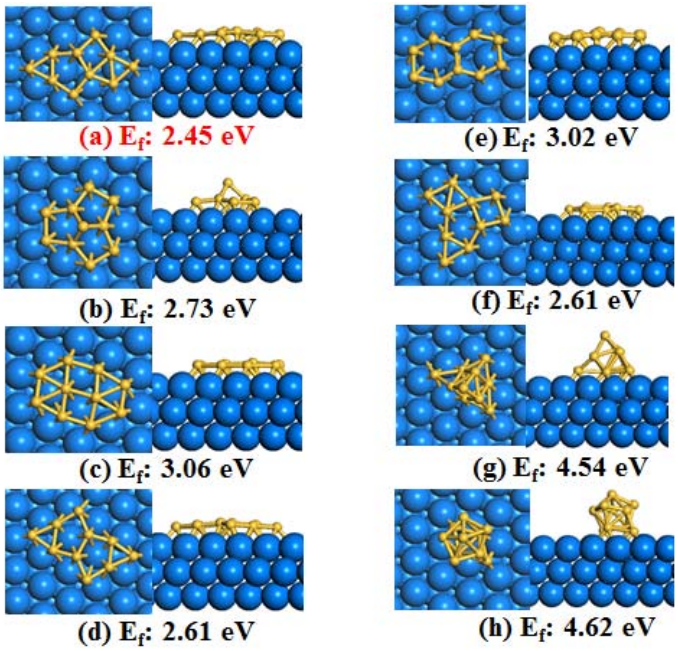

Fig. S1. Geometries and formation energies of eight optimized Si_{10} clusters on Ag(111) surface. The ground-state structure is highlighted by the red label.

Fig. S1a-S1h shows eight optimized Si_{10} clusters and their corresponding formation energies. The optimized Si_{10} clusters include six planar network structures and two polyhedral structures (Fig. S1g and S1h), the Si chains have not been considered due to their relatively higher formation energies. As shown in Fig. S1, the planar network structures are energetically favorable but the polyhedral structures are unstable for the Si_{10} clusters. The similar phenomenon has been observed in other sized Si clusters.

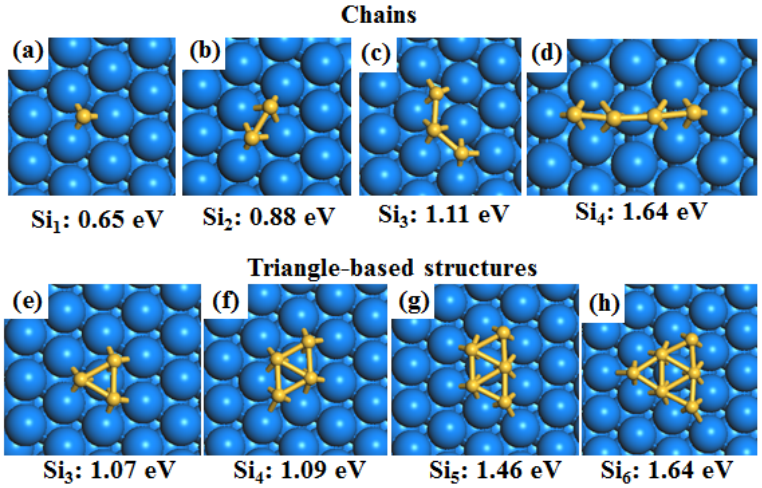

Fig. S2 Geometries and formation energies of Si_N chains and planar triangle-based structures on Ag(111) surface ($1 \leq N \leq 6$).

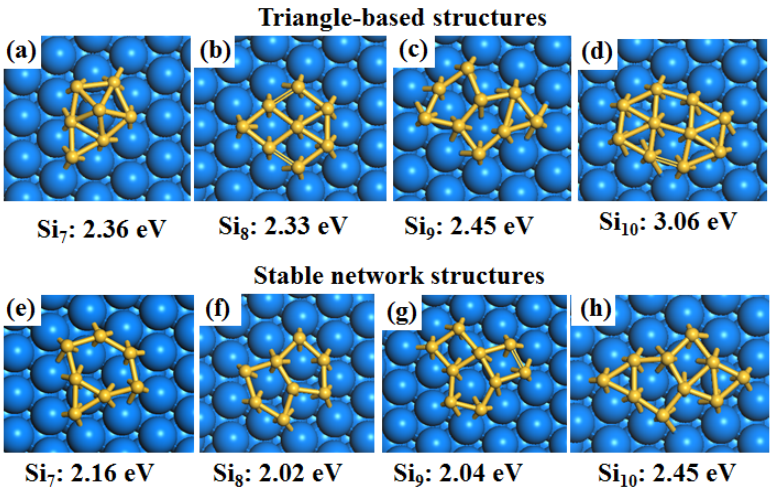

Fig. S3 Geometries and formation energies of Si_N ($7 \leq N \leq 10$) planar clusters on Ag(111) surface. The upper and lower panels in this figure indicate the triangle-based and stable network structures, respectively.

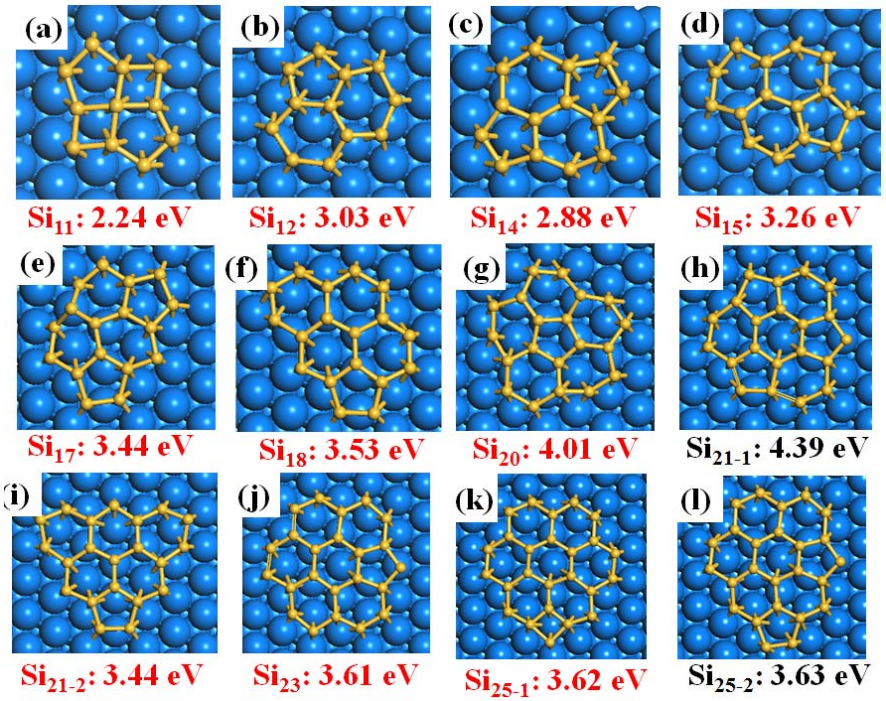

Fig. S4. Geometries and formation energies of Si_{11}~Si_{25} clusters on Ag(111) surface. The ground-state structures are highlighted by the red labels.

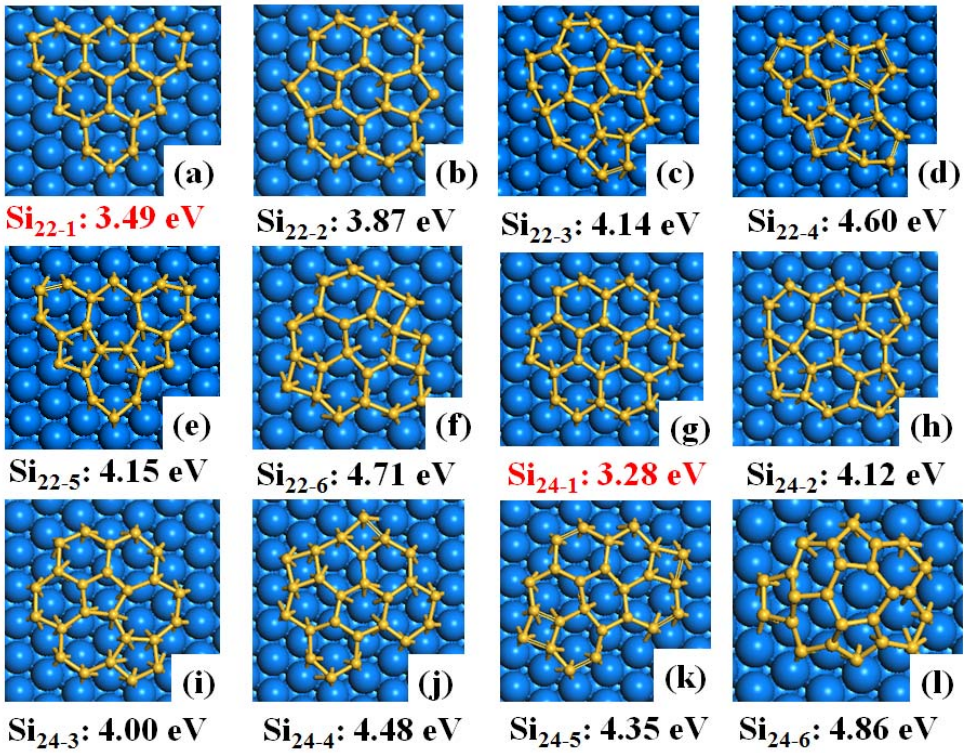

Fig. S5. Geometries and formation energies of Si_{22} and Si_{24} isomers on Ag(111) surface. The ground-state structures are highlighted by the red labels.

The calculations for the nucleation rate of silicene on Ag(111) surface

According to the classical crystal nucleation theory, the two-dimensional (2D) nucleation rate is defined as follows[2],

$$R_n = \omega \Gamma N_c \exp(\Delta G^*/k_B T) = R_0 \exp(\Delta G^*/k_B T) \quad (1)$$

where ω is the attachment rate of Si atoms into a critical silicene nucleus, $\Gamma = [\Delta G^*/(4\pi k_B T N^{*2})]^{1/2}$ is the Zeldovich factor, and N_c is the concentration of atoms/molecules. To obtain the nucleation rate of silicene on Ag(111) surface, the prefactor R_0 needs to be estimated firstly. The attachment rate ω can be calculated by

$$\omega = N_{edge} p(v \exp(\Delta G^*/k_B T)) \quad (2)$$

where N_{edge} is the number of attachment sites of the 2D nucleus. For a planar 2D network structure, $N_{edge} \sim (6\times N^*)^{1/2} \sim 10$, and $v = 10^{13}\ s^{-1}$. E_b is estimated approximately as the diffusion barrier of Si atom along Ag(111) surface, which is ~ 0.12 eV. p is the occupancy rate that is approximately equal to N_c. Based on the previous experimental studies[3,4], the concentration of Si monomer atoms on Ag(111) surface is about 0.05 monolayer (ML) silicene. Thus, the concentration of Si atoms N_c is ~ 0.783 nm^{-2} and p is ~ 0.05. The temperature T is referred to the typical growth temperature of silicene on Ag(111) surface, ~ 500 K. Taking the parameters into eq. (1) and eq. (2), the prefactor R_0 can be determined.

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