Electronic supplementary information

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

Haibo Shu,*a,b Dan Cao,c Pei Liang,a Xufeng Jing,b Xiaoshuang Chen,b and Wei Lu,b

a College of Optical and Electronic Technology, China Jiliang University, 310018 Hangzhou, China
b National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Science, 200083 Shanghai, China
c College of Science, China Jiliang University, 310018 Hangzhou, China

*Corresponding authors. E-mail: shu123hb@gmail.com

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 ≤ N ≤ 6).

Fig. S3 Geometries and formation energies of Si$_N$ (7 ≤ N ≤ 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\(^2\),

\[
R_n = \omega \Gamma N_c \exp(\Delta G^*/k_BT) = R_0 \exp(\Delta G^*/k_BT)
\]

(1)

where \(\omega\) is the attachment rate of Si atoms into a critical silicene nucleus, \(\Gamma = [\Delta G^*/(4\pi k_BT N^*)^{1/2}]\) 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 \(\omega\) can be calculated by

\[
\omega = N_{\text{edge}} p(\nu \exp(\Delta G^*/k_BT))
\]

(2)

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

REFERENCES