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Full Length Article

Temperature and coverage effects on the stability of epitaxial silicene on Ag(111) surfaces

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ABSTRACT

Silicene, the single layer of silicon atoms arranged in a honeycomb lattice, has been synthesized in recent experiments and attracted significant attentions. Silicene is promising in future nanoelectronic devices due to its outstanding electronic properties. In experiments, however, different silicene superstructures coexist on Ag(111) substrate. For the device applications, homogenous silicene sheet with large scale and high quality is highly desired. Here, for the first time, we investigate both the temperature and the coverage effects on the thermal stability of epitaxial silicene on Ag(111) surface by *ab initio* molecular dynamics simulations. The relationship between the stability of various silicene superstructures and the growth conditions, including temperature and coverage of silicon atoms, is revealed by plotting the chemical potential phase diagram of silicene on Ag(111) surfaces at different temperatures. Our results are helpful for understanding the observed diversity of silicene phases on Ag(111) surfaces and provide some useful guidance for the synthesis of homogenous silicene phase in experiments.

1. Introduction

Silicene, a counterpart of graphene, has attracted tremendous attentions due to its excellent electronic properties and potential applications in silicon-based microelectronics [1–8]. The first attempt to single layer of Si atoms traces back to the year of 1994 [9], while low-buckled silicene was confirmed to be dynamically stable until 2009 by Ciraci's group via phonon dispersion calculations and *ab initio* molecular dynamics (AIMD) simulations [10]. Similar to graphene, silicene also exhibits semimetal character with linear band dispersion near the Fermi level, forming the famous "Dirac cone" [10,11]. Superior to graphene, the spin-orbit coupling (SOC) effect in silicene is much stronger due to the heavier atomic mass of Si than C. Therefore, the quantum spin Hall effect (QSHE) in silicene is more prominent than that in graphene [12]. Owing to its buckled geometry, the band gap of silicene can be effectively tuned by a perpendicular electric field [13]. In addition, the band gap of silicene can be easily opened via chemical modification, such as hydrogenation [14–17], oxidation [18,19], halogenation [20,21], metal adsorption [22] and intercalation [23]. This is crucial for the application of silicene in future nanoelectronic devices since an appropriate band gap is needed to realize a high current on/off ratio in field effect transistors [24].

Due to the outstanding properties and potential applications of silicene, plenty of efforts have been devoted to fabricating silicene in experiments. Up to now, silicene has been epitaxially synthesized on various metal surfaces (ZrB_2(0001), ZrC(111) and Ir(111)), especially on Ag(111) [25–34]. According to the lattice match between silicene and Ag(111), several silicene superstructures including (4×4), $(\sqrt{13}\times\sqrt{13})R13.9^\circ$ and $(2\sqrt{3}\times2\sqrt{3})R30^\circ$ can form on Ag(111) surface [25–27,29,31,35], which can be viewed as the same silicene layer on Ag(111) surface with different buckling patterns due to different rotation angles relative to the silver substrate. However, the quality of the epitaxial silicene sheets is usually not satisfactory. Defects are frequently observed in the epitaxial silicene [29,35–43], which may affect the intrinsic properties of silicene significantly [44]. Moreover, it is difficult to synthesize large-scale silicene sheet with homogeneous phase [26,29,31,35].

Experiments indicate that both the temperature of the substrate and the coverage of silicon atoms have prominent effects on the stability of silicene superstructures on Ag(111) surface [27,29,31]. In a previous experiment by Chiappe et al. [29], the coverage effect was explored by fixing the substrate temperature at 520 K. It turned out that deposition of silicon atoms with silicon coverage $\theta\approx0.45$ monolayer (ML) results in no silicene structure. By increasing the coverage ($\theta\approx0.65$ ML), small silicene domains with (4×4) and $(\sqrt{13}\times\sqrt{13})$ superstructures coexist on the Ag surface. More-

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over, Wu's group found that $\sqrt{13}\times\sqrt{13}$ silicene prefers to form at a lower Si coverage and slightly lower temperature as compared with 4×4 silicene [27]. For the three frequently observed phases of silicene, (4×4) and $(\sqrt{13}\times\sqrt{13})$ phases always coexist [26,29,31,35], implying the comparable stability of these two phases; while $(2\sqrt{3}\times2\sqrt{3})R30^{\circ}$ usually occurs at a high silicon coverage and high temperature [27,31].

Clearly, understanding the growth mechanism is crucial for improving the quality of silicene sheets. Some theoretical efforts have already been devoted to exploring the growth mechanism of silicene in the early stage of nucleation and growth [45,46] and the coverage dependent stability of different superstructures of silicene [47]. However, an atomistic picture of the temperature and coverage effects on the growth behavior of silicene has not been established yet. In this work, we investigate the influence of both temperature and coverage on the thermodynamic stability of Ag(111)-supported silicene with;1; different superstructures by AIMD simulations. By constructing a chemical potential phase diagram, we disclose that $\sqrt{13}\times\sqrt{13}$, 4×4 and $2\sqrt{3}\times2\sqrt{3}$ silicene phases prevail in turn as the silicon supply increases from poor to rich. Temperature also plays a vital role on the relative stability between $\sqrt{13}\times\sqrt{13}$ and 4×4 silicene. Our theoretical results for the first time elucidate the temperature and coverage effects on the epitaxial silicene and provide useful guidance for the synthesis of silicene with single phase in future experiments.

2. Computational method

Ab initio molecular dynamics (AIMD) simulations were carried out using the Vienna Ab Initio Simulation Package (VASP) based on density functional theory (DFT) [48]. The projector augmented wave (PAW) potentials were adopted to describe the electron-ion interactions [49]. The exchange and correlation interaction was described by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [50]. A kinetic energy cutoff of 400 eV for the plane wave basis and a convergence criterion of 10^{-5} eV for the total energies were adopted throughout the DFT calculations.

The Ag(111) surface was modeled by a three-layer slab model with a vacuum space of more than 12 Å, which was cleaved from bulk face-centered-cubic (fcc) silver with the experimental lattice constant of 2.89 Å. With constrained lattice constants, the Ag(111) slab model was further relaxed, with the bottom atomic layer fixed to mimic a semi-infinite solid. Following our previous work [45], here we built three kinds of silicene superstructures on the Ag(111) surface, i.e. 3×3 silicene on a 4×4 Ag(111) surface (denoted as 4×4 silicene thereafter), $\sqrt{7}\times\sqrt{7}$ silicene on $\sqrt{13}\times\sqrt{13}$ Ag(111) surface (denoted as $\sqrt{13}\times\sqrt{13}$ silicene thereafter), and $\sqrt{7}\times\sqrt{7}$ silicene on $2\sqrt{3}\times2\sqrt{3}$ Ag(111) surface (denoted as $2\sqrt{3}\times2\sqrt{3}$ silicene thereafter), by compressing or stretching the silicene lattice slightly to fit the metal surface. 2×2 supercells were used in the MD simulations for all the three silicene superstructures. Hence, the lattice constants of the supercells in our MD simulations were 23.12 Å, 20.83 Å and 20.04 Å for 4×4, $\sqrt{13}\times\sqrt{13}$ and $2\sqrt{3}\times2\sqrt{3}$ silicene, respectively, corresponding to $Si_{72}Ag_{192}$, $Si_{56}Ag_{156}$ and $Si_{56}Ag_{144}$, respectively.

AIMD simulations were performed within the NVT ensemble with a time step of 1 fs and a total simulation time of 10 ps at each temperature. The system temperature was controlled by the algorithm of Nosé [51,52]. During the AIMD simulations, the bottom layer of Ag(111) slab was also fixed. Typically, thermal equilibrium can be reached within the initial simulation time of 4 ps. We then lasted for another 6 ps to sample the time-averaged free energy. To characterize the thermal stability of the Ag(111)-supported silicene (or Ag(111) surface itself), we monitored the thermally induced disorder given by the Lindemann index δ:

$$\delta = \frac{1}{n(n-1)}\sum_{i}\sum_{j\neq i}\frac{\sqrt{\langle r_{i,j}^2\rangle - \langle r_{i,j}\rangle^2}}{\langle r_{i,j}\rangle}, \quad (1)$$

where n is the number of silicon atoms in Ag-supported silicene (or Ag atoms in the upper two Ag layers) and $r_{i,j}$ is the distance between the i^{th} atom and the j^{th} atom in silicene (or the upper two Ag layers). Angle brackets indicate a time average over the AIMD simulation.

3. Results and discussion

We start from investigating the thermal stability of Ag(111) surface itself. As shown in Fig. S1a of Supplementary material, the structure of Ag(111) surface after 10 ps AIMD simulation becomes disordered at 900 K, implying the occurrence of surface melting of the silver substrate. In addition, the Lindemann index of Ag(111) surface as a function of temperature (see Fig. S1b of Supplementary material) shows a sharp increase from 900 K to 1000 K, further confirming the surface melting of the silver substrate at 900 K. Our current result agrees well with the previous Monte Carlo simulation with Gupta potential, which predicted the surface melting of Ag(111) surface at about 1000–1050 K [53]. Previous DFT calculations show that Si atoms can penetrate the topmost layer of Ag surface by overcoming an energy barrier [54]. In such way, Si atoms can easily enter the Ag(111) substrate at 900 K due to the surface melting of the Ag substrate. Indeed, when the substrate temperature is over 600 K, no silicene would form and there is only a bare Ag(111) surface left [27,31]. Note that the surface melting point of the Ag substrate should not be the critical temperature for the disappearance of silicene layers since the surface melting of the Ag substrate is not necessary for Si atoms to penetrate into Ag surface.

As the most frequent phases of silicene on Ag(111) surfaces, here we consider three silicene superstructures, i.e., 4×4, $\sqrt{13}\times\sqrt{13}$ and $2\sqrt{3}\times2\sqrt{3}$. Their optimized atomic structures are shown in Fig. S2 of Supplementary material. In view of the surface melting of the Ag substrate at 900 K, the temperatures for MD simulations of these silicene/Ag systems range from 400 K to 800 K with an increment of 100 K. After 10 ps MD simulation at 400 K, the structures of all the three silicene phases show no substantial difference from the optimized structures at 0 K except for the buckle pattern as depicted in Fig. S3 of Supplementary material. As shown in Fig. 1, the honeycomb structure of silicene is well preserved even at 800 K. No defects ever occurred during the entire MD simulation of 10 ps for all the three silicene phases. This observation indicates the high stability of silicene on Ag(111) surface, which can be attributed to the moderate and uniform interaction between silicene and the Ag substrate [45].

To further confirm the thermal stability of silicene on Ag(111) surface, we calculate the Lindemann index of Ag(111)-supported silicene using Eq. (1). The Lindemann indexes of different silicene superstructures as functions of temperature are displayed in Fig. 2. The Lindemann indexes of all three silicene phases increase slowly with the increasing of temperature, implying that these silicene structures do not suffer severe destruction even at 800 K. However, in experiments if the silicene sample on Ag(111) is annealed up to 600 K, silicene film would disappear [27]. This can be probably ascribed to the existence of structural defects [29,35-43], which can reduce the thermal stability of silicene considerably [55].

In order to compare the thermodynamic stabilities of different silicene structures on Ag(111) surface, we calculate their Gibbs free energies. In experiments, silicene is usually synthesized by molecular beam epitaxy (MBE) method. Si atoms are deposited on