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Abstract

We report on the epitaxial growth mechanism of silicene layers fabricated on a Ag(111) surface by molecular beam epitaxial deposition. The coverage effect and the structural defects have been characterized using scanning tunneling microscopy (STM). It is found that substrate temperature plays an important role in the formation of silicene in different structures. Several kinds of defects are observed in different phases of silicene, which are most likely induced by the low coverage effect and the structural mismatch between the silicene and the Ag(111) surface. The Silicene sheet prefers to first emerge at the terrace edge of the substrate. Our results indicate that the growth mechanism of silicene follows the Stranski-Krastanov growth mode for all structures.

Keywords

growth, epitaxial, mechanism, 111, silicene, ag

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Epitaxial growth mechanism of silicene on Ag(111)

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Abstract— We report on the epitaxial growth mechanism of silicene layers fabricated on Ag(111) surface by molecular beam epitaxial deposition. The coverage effect and the structural defects were characterized by using scanning tunneling microscopy (STM). It is found that substrate temperature plays an important role in the formation of silicene in different structures. Several kinds of defects are observed in different phases of silicene, which are most likely induced by the low coverage effect and the structural mismatch between the silicene and the Ag(111) surface. Silicene sheet prefers to emerge firstly at the terrace edge of substrate. Our results indicate that growth mechanism of silicene follows the Stanski-Krastanov growth mode for all structures.

Keywords— *silicene; epitaxial; STM; growth mechanism; defect; coverage*

I. INTRODUCTION

Due to the unique nanostructures and electronic states, two-dimensional (2D) materials play a pivotal role in innovative concepts and pioneering applications. Recently, a novel silicon-based 2D single-atom layer, namely, silicene, has attracted intensive interest because it is an ideal candidate material for promising applications in electronics, photonics, and the other related areas [1-3]. The theoretical simulations show that silicene has the similar electronic band structure with graphene and is a new massless Dirac Fermion system [4, 5], which has been experimentally proved by observation of linear behavior of energy-momentum dispersion and a large Fermi velocity⁶. Silicene shows a large spin-orbit coupling, which may allow a large energy gap at the Dirac point and result in a detectable quantum spin Hall (QSH) effect, and inherent compatibility with the current semiconductor industry [5-8]. In addition, unlike graphene sheets which are chemical inert at surface, silicene sheets demonstrate high chemical activity which potentially makes their physical, chemical and electronic properties easily being modulated by chemical functionalization [9]. Although it has been proposed that the substrate temperature and the surface coverage play an important role in the formation of silicene in different phases¹, few works studied the growth mechanism and the origin of the defects in epitaxial silicene, which is highly desirable before fabrication of large-scale high-quality silicene layers for applications.

In this work, we investigate the epitaxial growth mechanism and defects in silicene in different phases. Single and multiple layered silicene sheets were obtained. It is found that the silicene sheets prefer to grow from the terrace edge of the silver substrate Ag(111) following Stanski-Krastanov (SK) growth mode.

II. EXPERIMENTS AND METHODS

All samples used in this work were *in-situ* prepared in a preparation chamber of a low-temperature scanning tunneling microscopy system (LT-STM) (SNOM1400, Unisoku Co.). A clean Ag(111) substrate was prepared by argon ion sputtering and with subsequent annealing at 550°C for several cycles. The silicene monolayers were fabricated by the evaporation of silicon from a heated silicon wafer. The deposition flux was 0.08 monolayers per minute (ML/min). The temperature of the Ag(111) substrate was 450 K, 500 K and 550 K for the formation of $\sqrt{13}\times\sqrt{13}$, 4×4 and $2\sqrt{3}\times2\sqrt{3}$ phases, respectively. The STM measurements were carried on in ultra-high vacuum (UHV, $<8\times10^{-11}$ torr) at room temperature. Before STM measurements, Pt/Ir tip was calibrated on a silver surface.

III. RESULTS AND DISCUSSION

Fig. 1 shows the STM images of silicene nanosheets in different phases, namely, $\sqrt{13}\times\sqrt{13}$, 4×4 and $2\sqrt{3}\times2\sqrt{3}$. When the substrate temperature is less than 450 K, the amorphous silicon film forms in the Ag(111) substrate, as shown in Fig. 1(a). It is found that the $\sqrt{13}\times\sqrt{13}$ phases with close-packed protrusions and the 4×4 phase always coexist on a large area of the silver surface (Fig. 1(b)) when the substrate temperature is between 450 K and 520 K. This coexistence indicates the similar formation energy of these two phases. It is noticeable that the periodicity of the two phases is almost the same (1.16 nm), which is also a vital factor for the coexistence of two phases. When substrate temperature is increased above 520 K, $2\sqrt{3}\times2\sqrt{3}$ phase forms with traces of 4×4 phase. The pure $2\sqrt{3}\times2\sqrt{3}$ phase silicene can be attained when the substrate temperature is higher than 550 K. The long-ranged ordered and well spread moiré pattern over the whole $2\sqrt{3}\times2\sqrt{3}$ silicene surface is shown in Fig. 1(c). The angle between honeycomb structure and the direction of moiré pattern is around 30°, which is in consistence to the previous reports [1].

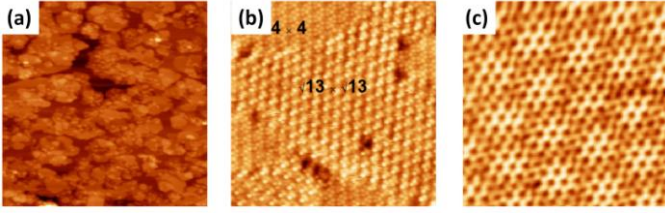


Fig. 1. (a) STM topography image of amorphous layer (scanning area $16\text{ nm}\times 16\text{ nm}$, $V_{\text{bias}} = 2.0\text{ V}$, $I = 0.1\text{ nA}$). (b) STM topography image of mixed two major phases of silicene, $\sqrt{13}\times\sqrt{13}$ and 4×4 , in different domains are labeled. (scanning area $16\text{ nm}\times 16\text{ nm}$, $V_{\text{bias}} = -0.4\text{ V}$, $I = 5\text{ nA}$). (c) STM images of $2\sqrt{3}\times 2\sqrt{3}$ phases of silicene (scanning area $16\text{ nm}\times 16\text{ nm}$, $V_{\text{bias}} = -0.8\text{ V}$, $I = 1.5\text{ nA}$).

Several types of defect are observed in different silicene phases. Fig. 2(a) displays the STM images of unordered stripes among the bright atom image. These stripe-like defects are caused by grain boundaries between $\sqrt{13}\times\sqrt{13}$ -I and $\sqrt{13}\times\sqrt{13}$ -II phases, which possess different atomic structure [10]. The topographic triangle defect, labeled by red arrow, is observed among 4×4 phase in Fig. 2(b). This triangle defect, which only displays in 4×4 phase but not in $\sqrt{13}\times\sqrt{13}$ and $2\sqrt{3}\times 2\sqrt{3}$ phases, is due to perfect honeycomb structure with the deficiency of several atoms in top layer, which is verified by STM images. It is attributed to that 4×4 silicene sheet has more Si atoms in top layer and less average binding energy with substrate per silicon atom compared with $\sqrt{13}\times\sqrt{13}$ phase and 4×4 phase [10]. The high-resolution STM image in Fig. 2(c) displays complete honeycomb rings with periodical lattice at the bright part of moiré pattern, and rather defective and distorted rings in the dark part of moiré pattern. Such phenomenon has been predicted to be caused by the lattice mismatch between the silicene sheet and silver substrate by density functional theory (DFT) simulations [3]. Silicon atoms at the bright part of moiré pattern are little deviated from the position of Ag(111), making structure stable enough to keep honeycomb rings. The large deviation in the dark part of moiré pattern, leads to unstable structure and eventually breaks the rings.

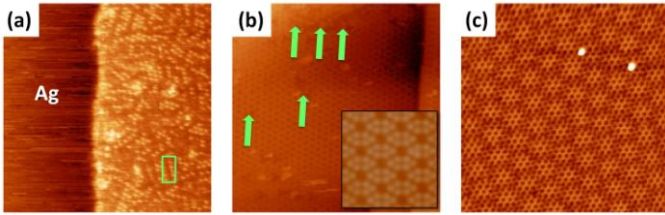


Fig. 2. STM images of (a) $\sqrt{13}\times\sqrt{13}$ phase of silicene with stripe-like defects labeled by rectangle (scanning area $32\text{ nm}\times 32\text{ nm}$, $V_{\text{bias}} = -1.2\text{ V}$, $I = 0.8\text{ nA}$), (b) 4×4 phase of silicene with triangle phase (scanning area $32\text{ nm}\times 32\text{ nm}$, $V_{\text{bias}} = -0.8\text{ V}$, $I = 0.5\text{ nA}$), (c) $2\sqrt{3}\times 2\sqrt{3}$ phase of silicene with distortion (scanning area $32\text{ nm}\times 32\text{ nm}$, $V_{\text{bias}} = -0.8\text{ V}$, $I = 1.5\text{ nA}$) on Ag(111). The green arrows in figure 2(b) label the position of triangle defects. Insert of (b) shows the enlarge view of 4×4 phase of silicene.

The growth mechanism of multi-layer silicene has been investigated by tuning Si coverage. The topographic images of amorphous and the $\sqrt{13}\times\sqrt{13}$ phase in the submonolayer are shown in Fig. 3(a) and (b), respectively. It demonstrates clearly that both structures are grown from terrace edge of silver substrate. When the coverage of silicene is more than 1 monolayer (ML), second layer emerges on the first layer of

silicene in the form of island. These islands prefer to locate in the terrace of first layer. The insert of Fig. 3(c) shows the enlarge view of the second layer. Both the amorphous and $\sqrt{13}\times\sqrt{13}$ phases are observed in the second layer. It should be noted that there is no trace of continuity between the first layer and second layer, indicating that the second layer grows when the first layer film completely forms on the silver substrate.

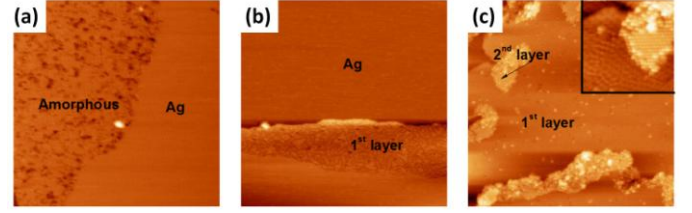


Fig. 3. (a) STM image of amorphous film in first layer (scanning area $80\text{ nm}\times 50\text{ nm}$, $V_{\text{bias}} = -1.2\text{ V}$, $I = 0.5\text{ nA}$). (b) STM image of $\sqrt{13}\times\sqrt{13}$ phase of silicene in first layer (scanning area $80\text{ nm}\times 80\text{ nm}$, $V_{\text{bias}} = -1.0\text{ V}$, $I = 0.5\text{ nA}$). (c) STM image of second layer of silicene (scanning area $80\text{ nm}\times 80\text{ nm}$, $V_{\text{bias}} = -1.2\text{ V}$, $I = 0.1\text{ nA}$). The insert of figure 3(c) is the enlarged view of the second layer grows on the top of first layer (scanning area $16\text{ nm}\times 16\text{ nm}$, $V_{\text{bias}} = -1.2\text{ V}$, $I = 0.1\text{ nA}$).

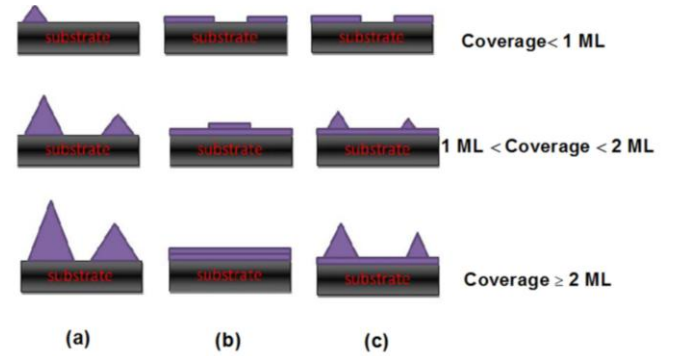


Fig. 4. Cross-section views of the three primary modes of thin-film growth including (a) Volmer-Weber (VW: island formation), (b) Frank-van der Merwe (FM: layer-by-layer), (c) Stranski-Krastanov (SK: layer-plus-island). Each mode is shown for several different amounts of surface coverage.

There are three epitaxial modes of thin film growth, which are Volmer-Weber (VW) mode, Frank-van der Merwe (FM) mode, and Stranski-Krastanov (SK) mode. As shown in Fig. 4(a), in VW growth mode, the films form in three dimensional adatom clusters or islands and cause rough multi-layer structures on the substrate surface. The FM growth mode, shown in Fig. 4(b), is a 2D layer-by-layer mode that leads to complete films formation prior to growth of subsequent layers. SK growth mode (Fig. 4(c)), is an intermediary process between 2D layer and 3D island growth. Transition from the layer-by-layer to island-based growth occurs at a critical layer thickness which highly depends on the chemical and physical properties such as surface energies and lattice parameters, of the substrate and film. Based on the observation of both the completely coverage of first layer and the fact that amorphous islands and $\sqrt{13}\times\sqrt{13}$ phase coexist in the second layer, it can be concluded that the silicene growth mechanism is belong to the SK mode, and the critical layer for the transition from 2D mode to 3D model is 1 ML.

IV. SUMMARY

In summary, we investigate the influence of substrate temperature on silicene structure and the growth mechanism in the different coverage levels. Defects in $\sqrt{13}\times\sqrt{13}$ phase are due to the grain boundary between different phases as well as the low coverage. Deficiencies of atoms in top layer form the defects in 4×4 phase, which is probably caused by the more atoms in top layer and weak bond between the top layer atom and silver substrate. The lattice mismatch between silicene and substrate induces the break and distortion in dark part of moiré pattern in $2\sqrt{3}\times 2\sqrt{3}$ phase. The study of topography of different layer silicene demonstrates that the silicene grows under the SK mode, which is not only to better understand the complex thermodynamics and kinetics at the core of silicene formation, but also a route to fabricating novel nanostructures for application in the microelectronics industry.

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