In situ SEM/STM observations and growth control of monolayer graphene on SiC (0001) wide terraces

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Abstract: Thermal decomposition of SiC is frequently used for the formation of graphene on semi-insulating substrates, but the growth mechanism is not well understood and thus the method to form monolayer graphene with larger domain size especially on step-free or wide terrace surfaces is not known. In this work, various stages of graphene growth on SiC (0001) during annealing at 1-atm-Ar atmosphere were observed by *in situ* SEM/STM. We found that a prolonged heating at 1550ºC over 1h brought about the growth of monolayer graphene, starting from step edges and continuously across the whole terrace without pit formation. Monolayer graphene with the domain size over 3 μm was fabricated on wide terraces, which covered more than 90% areas of the sample surfaces.

Keywords: epitaxial graphene, SiC (0001), growth control, SEM, STM

1. Introduction

Graphene is a one-atom-thick sheet of carbon atoms arranged in a honeycomb lattice. The unique electric properties [1-4] make graphene the most ideal two-dimensional material for next generation electronics [5-8]. Epitaxial growth of graphene on silicon carbide (SiC) is an approach to form graphene directly on insulating substrates. High quality epitaxial graphene has been easily formed on SiC (0001) surfaces by suppressing the sublimation of Si atoms in inert gas atmospheres [9] or Si background [10]. However, morphology of SiC surfaces after graphene growth is complicated and highly depends on the annealing conditions. Several groups have proposed different growth models in previous studies [11-13], which are speculations based on their own observations at final state of the graphene growth on SiC and still confuse us.

As a matter of fact, step edges on SiC surfaces play an important role in providing carbon atoms for the graphene growth. Sun *et al.* [14] reported that the SiC surfaces with abundant steps were necessary to fabricate pit-free graphene on SiC substrates. Nevertheless, the steps prevent graphene from growing to large domains, due to increasing graphene nucleus density at the step edges, as shown in Fig. 1(a). On the other hand, for the case of step-free surfaces or the center of wide terraces (Fig. 1(b)), graphene nucleates both from step edges and on terraces. Abundant decomposed Si atoms on terraces will break the first buffer layer with forming pits, leading to discontinuous growth of monolayer graphene.

In this work, in order to investigate the behavior of graphene growth on step-free SiC surfaces, we prepared SiC samples with wide terraces for epitaxial growth of graphene. The surface morphologies after graphene growth were observed by in situ ultra-high vacuum scanning electron microscopy and scanning tunneling microscopy (UHV-SEM/STM) system. We successfully captured several sequential series of SEM images at various stages of monolayer graphene growth at the same portions on SiC surface. This work sheds light to the growth process of large-scale graphene on SiC surfaces.

2. Experimental

Single-crystalline n-type 6H-SiC substrates were cut to a size of 12×3×0.33 mm. The Si-terminated faces of the substrates were polished by a chemical-mechanical planarization method (CMP) with a miscut angle of ±0.5º. As a pretreatment of the samples, SiC substrates were firstly cleaned in acetone by an ultra-sonic cleaner to remove impurity on samples' surface. After that the samples were fixed in a heating sample holder made of molybdenum and transferred into UHV-SEM/STM system. Then the sample surfaces were etched in 0.1-atm-hydrogen atmosphere at 1300ºC for 15 mins to remove adsorbates such as water and oxygen. In order to identify the same position on a sample surface after various annealing stages by SEM, the SiC surface was patterned to make markers by laser lithography and reactive ion etching (RIE). The patterned surface showed mesas with a height of 60 nm under the etch condition of CF_4 (40 sccm) / O_2 (20 sccm) mixture at a power of 200 W for 1 min [15].

Thermal annealing of SiC substrates and characterization of their surfaces were carried out by using an Omicron UHV-SEM/STM apparatus with a customized preparation chamber, where a sample can be annealed in various atmospheres (UHV to 1atm) and observed by reflection high-energy electron diffraction (RHEED). Thermal annealing of SiC substrates was carried out in a range of temperature from 1300 to 1600ºC in an Ar atmosphere at 1 atm. The annealed samples can be directly transferred to the main chamber for SEM and STM observations without exposing to the air.

3. Results and discussion

3.1 Monolayer graphene growth on wide terraces

Annealing of SiC substrates in 1-atm-Ar atmosphere above 1400ºC brings about step bunching, and formation of graphene layers was observed at 1550ºC. At higher temperatures, graphene grew faster and the nuclei in pits on terraces also formed due to the rapid decomposition of SiC. Under the 1-atm-Ar atmosphere, the SiC substrates have to be heated up to 1550ºC at the lowest to from a graphene layer. Thus, in order to grow graphene slowly, we adopted 1550ºC as the annealing temperature for graphene growth.

Figure 2(a) shows a SEM image of graphene grown on wide terraces over 3 μm in width by annealing at 1550ºC for 60 mins. Dark bands shown by white arrows are bunched step edges, where multilayer graphene are formed. As shown in Fig. 2(b), large gray regions on the terraces are monolayer graphene. Also striped buffer layer remained on the terraces with bright contrast. Such type of buffer layer, also known as the fingerlike buffer layer [13], is a typical feature of monolayer graphene grown from step edges, indicating that all the monolayer graphene on the terraces was grown from the step edges. Notably, the striped buffer layer is elongated in the direction of $\langle\bar{1}2\bar{1}0\rangle$ of SiC substrate. Figure 2(c) shows a high resolution STM image of monolayer graphene region. This image was scanned with 2048$\times$2048 pixels over an area of 800$\times$800 nm^2, such that a clear moiré pattern, as show in the insert, was observed in the entire region. Several vacancy defects can be found in this area (insert (c-1) in Figure 2(c)), which is common for epitaxial graphene on SiC [16], but no domain boundary was detected. Since the regions of monolayer graphene in other STM images also showed the same features, we consider that monolayer graphene grown from step edges forms as one domain. We can see that the annealing at 1550ºC makes graphene nucleate only at the step edges and slowly grow toward the center of a terrace over 3 μm in one domain. Monolayer graphene formed at such condition covered more than 90% area of the SiC surface, as observed by SEM.

In addition, buffer layer area has a lower height than graphene area in STM image (Figure 2(c)). However, due to the difference of electric properties, the height change between graphene and buffer layer cannot be indicated by STM. Actually, buffer layer areas are at higher positions, which are confirmed by AFM image in Figure 2(d). As known for the bottom-up growth process of graphene on SiC, graphene forms from the first buffer layer when underneath 3 SiC bilayers are etched on 6H-SiC substrates [17, 18, 19]. As shown by the profiles in Figure 2(d), striped buffer layer areas are about 0.4 nm higher than graphene areas on a terrace, indicating that the height difference (0.4 nm) is due to the decomposition of three SiC (0.75 nm) bilayers and the growth of a graphene layer (0.33 nm). Interestingly, a 1-nm-height difference is observed between the remained buffer layer and the front of grown graphene (see A-B profile in Figure 2(d)), which means that 6 SiC bilayers have been etched and one graphene layer has grown. The 1-nm-height difference has not been observed in previous reports [17, 18, 19]. One possible reason for the 6-bilayer etching is that 6 bilayers are decomposed easier from bunched step edges (about 10 nm height).

3.2 Graphene growth process at 1550ºC

In order to make clear how monolayer graphene grows from the step edges on wide terraces and why such stripe buffer layer forms during graphene growth, we investigated the whole processes of the graphene growth on the wide terraces. The patterned SiC substrate was annealed repeatedly at 1550ºC for 15 min serval times under 1-atm-atmosphere of Ar. After each annealing step the sample was cooled to room temperature and transferred to the main chamber for SEM observation. Figures 3(a, c, e and g) show a series of SEM images of monolayer graphene growth from step edges on this sample (the same position is marked by downward triangles). Graphene firstly formed uniformly over a width of 500 nm from step edges after annealing for 30 min as shown in Fig. 3(a). By subsequent annealing, the fingerlike morphology of a buffer layer started to form when graphene grew 800 nm from step edges (Fig. 3(c)). After that, the fingers shrank and disappeared when the growth front of graphene reached the next step as shown in Figs. 3(e and g). Although multilayer graphene grew at step edges as well, its growth speed was much slower than the monolayer graphene growth on terraces.

Borovikov *et al*. also observed the formation of striped buffer layer during the graphene growth under a background Si pressure [13]. They explained such phenomenon as a result of a curvature driven mechanism for step edge stability. The decomposition rate of SiC is higher for concave regions and lower for convex regions, such that the fingerlike buffer layer forms from a step edge at the beginning of graphene growth. According to our observation, the striped buffer started to form after the monolayer graphene uniformly grew over a width of 800 nm from the step edges, which cannot be explain by their mechanism. We assume that such striped buffer layer played a role as pathways of the decomposed Si atoms during the graphene growth on terraces, which well explain our observations, as illustrated in Figs. 3(b, d, f and h). As mentioned above, the monolayer graphene layer is formed from the first buffer layer when a new buffer layer grows due to the decomposition of underneath SiC. SiC decomposes at the front of new buffer layer and Si atoms have to diffuse between the monolayer graphene and the new buffer layer to the step edges for their sublimation. At the first stage, graphene grows near the step edges and the decomposed Si atoms can easily arrive at the edges as shown by blue arrows (Figs. 3(b and i)). The maximum width of uniform graphene band on the step edge (i.e. 800 nm) is considered to correspond to a diffusion length of the Si atoms. As graphene grows beyond the diffusion length of Si atoms, the diffusion of Si atoms may occurs through a gap under the graphene-buffer boundary as a pathway to the step edge (Figs. 3(d and j)). Then the decomposition of SiC under the striped buffer layer was suppressed by the supply of passing Si atoms, leaving the striped buffer layer even after the graphene covered over the whole terraces. Also the orientation of striped buffer layer in $\langle\bar{1}2\bar{1}0\rangle$ directions indicates that Si atoms diffuse easily in these directions. Finally, the striped buffer layer became narrow and disappeared from the back region of a terrace as shown in Figs. 3(f and h).

3.3 Starfish-like graphene nucleation

A new type of nucleation of monolayer graphene with a starfish-shape was observed on terraces as indicated by black arrows in Fig. 4(c). Before the appearance of the starfish-like nucleus, ordinary graphene growth from a step edge was observed as shown in Figs. 4(a and b). The starfish-like graphene nucleates on a terrace and grows branches in $\langle\bar{1}2\bar{1}0\rangle$ directions as shown in Fig. 4(c). After that, both the graphene nuclei at the step edge and on the terraces grew wider and finally contacted to each other, as shown in Fig. 4(d). Being different from the case of graphene growth from step edges, irregular-shaped buffer layer islands (Fig. 4(e)) were left in the graphene areas grown from the starfish-like nuclei.

Figure 5 shows SEM and STM images of a same area of the sample after the graphene had covered the whole terrace. Two graphene areas can be distinguished in the SEM image; one is graphene grown from the step edge, and the other, graphene formed from the starfish-like nuclei. The former includes the striped buffer layer, and the latter includes buffer layer islands with irregular shapes. Bolen et al. [20] reported similar observations of graphene islands in the pits on terraces of 4H-SiC substrates. For our case, no pit was formed at the terrace as shown in Fig. 5(a), which clearly differs from the previously reported graphene growth on a terrace by forming pits (Fig. 1). As is mentioned above (Figure 2(c-1)), vacancy defects exist in epitaxial graphene, so that we suggest such starfish-like graphene is formed due to the diffusion of decomposed Si atoms from a defect. Si atoms diffuse in $\langle\bar{1}2\bar{1}0\rangle$ directions and reach the defects for sublimation, such that the monolayer graphene could nucleate and grow on the terraces without forming pits. Hexagonal depression areas with a depth of one SiC bilayer are revealed by STM (bright arrows in Fig. 5(b)). However, no corresponding contrast shows out in the SEM image, indicating that monolayer graphene grew continuously in these areas. Also notably, no domain boundary was observed between the two graphene regions in STM image (Fig. 5(b)), suggesting that graphene areas grown on the terrace and from the step edge are connected as one domain without pit formation. Annealing at 1550ºC under an Ar pressure of 1 atm is the condition that SiC decomposes slowly from step edges and on terraces without damaging the first buffer layer. This process of monolayer graphene growth might be significant for the large domain graphene growth on completely step-free SiC surfaces.

4. Conclusion

In summary, during the study of graphene growth on SiC (0001) in our UHV-SEM/STM system, we found that 1550ºC is the temperature at which monolayer graphene slowly grow on wide terraces as one domain without pit formation. We also succeeded in recording the structure changes of a SiC surface during the graphene growth at the same location on a wide terrace by in situ SEM. According to the observation, the formation of fingerlike buffer layer is considered to be a result of the diffusion of Si atoms between a monolayer graphene and a newly formed buffer layer. In addition, a new type of starfish-like graphene nucleation was observed on the terraces. The two graphene regions nucleated from a step-edge and on a terrace were finally connected to form a large domain of graphene covering the wide terraces without pit formation.

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Figure captions

Figure 1 Schematic diagrams of graphene growth by thermal decomposition of SiC (a) on a stepped surface and (b) on a step-free or wide terrace surface.

Figure 2 (a) SEM images of graphene on a SiC substrate after annealed at 1550ºC for 60 mins; (b) zoomed image of the black frame in (a); (b) STM image (800×800 nm, bias voltage V_b=0.1 V, tunneling current I_t=0.1 nA) of the same sample. The inserts (c-1 and c-2) are enlarged images of monolayer graphene in (c). (d) AFM image and height profiles of graphene growth from step edges.

Figure 3 (a, c, e, g) A series of SEM images of graphene growth from step edges at 1550ºC. Time in the upper right represents duration of annealing time. (b, d, f, h) Schematic diagrams at different stages of the growth corresponding to (a, c, e, g). (i, j) Schematic diagrams of cross section of A-B in (b) and C-D in (d). Blue arrows in the schematic diagrams indicate the pathways of released Si atoms between monolayer graphene and a newly formed buffer layer.

Figure 4 (a-e) A series of SEM images of starfish-like graphene nucleation on terraces after the sample annealed for 30 to 90 mins; (f) an enlarged view of the black frame in (c).

Figure 5 (a) A SEM image and (b) a STM image (V_b=0.1V, I_t=0.1nA) scanned over the black framed area of the sample after annealed for 90 mins.

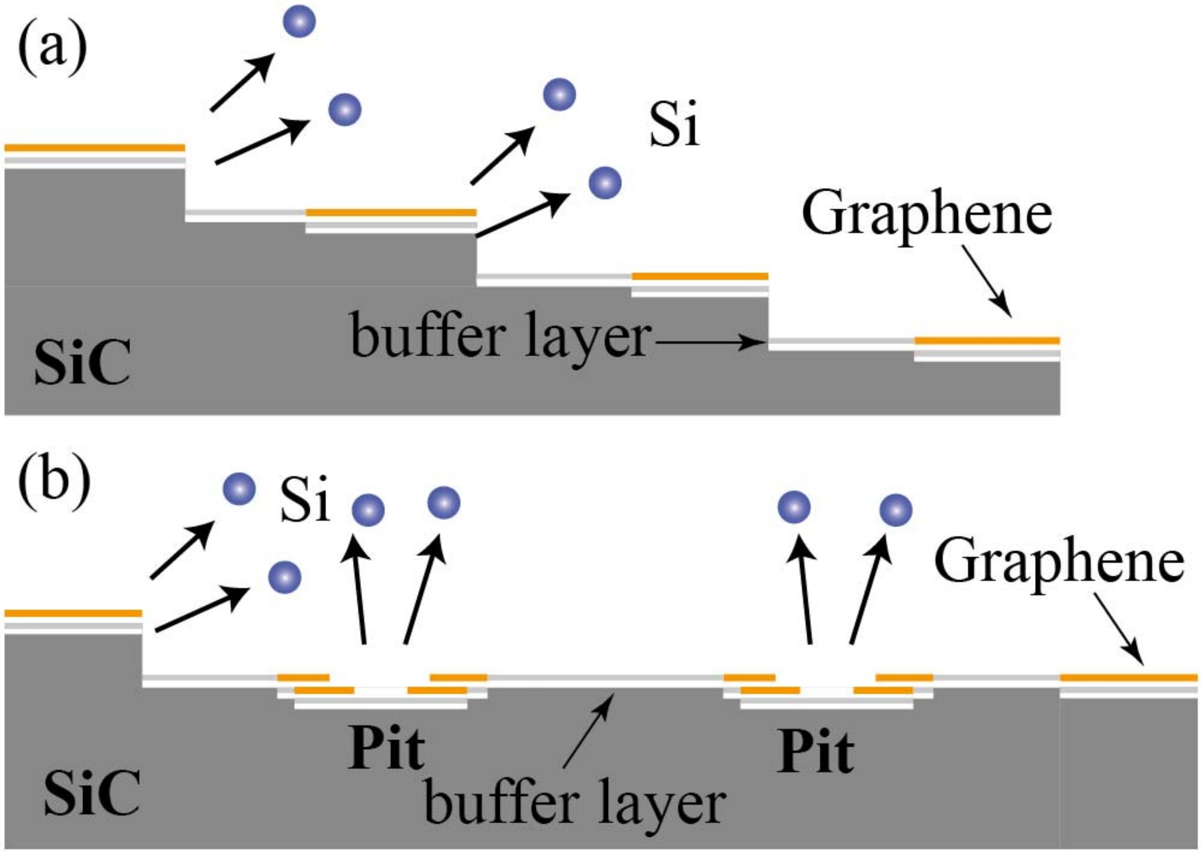
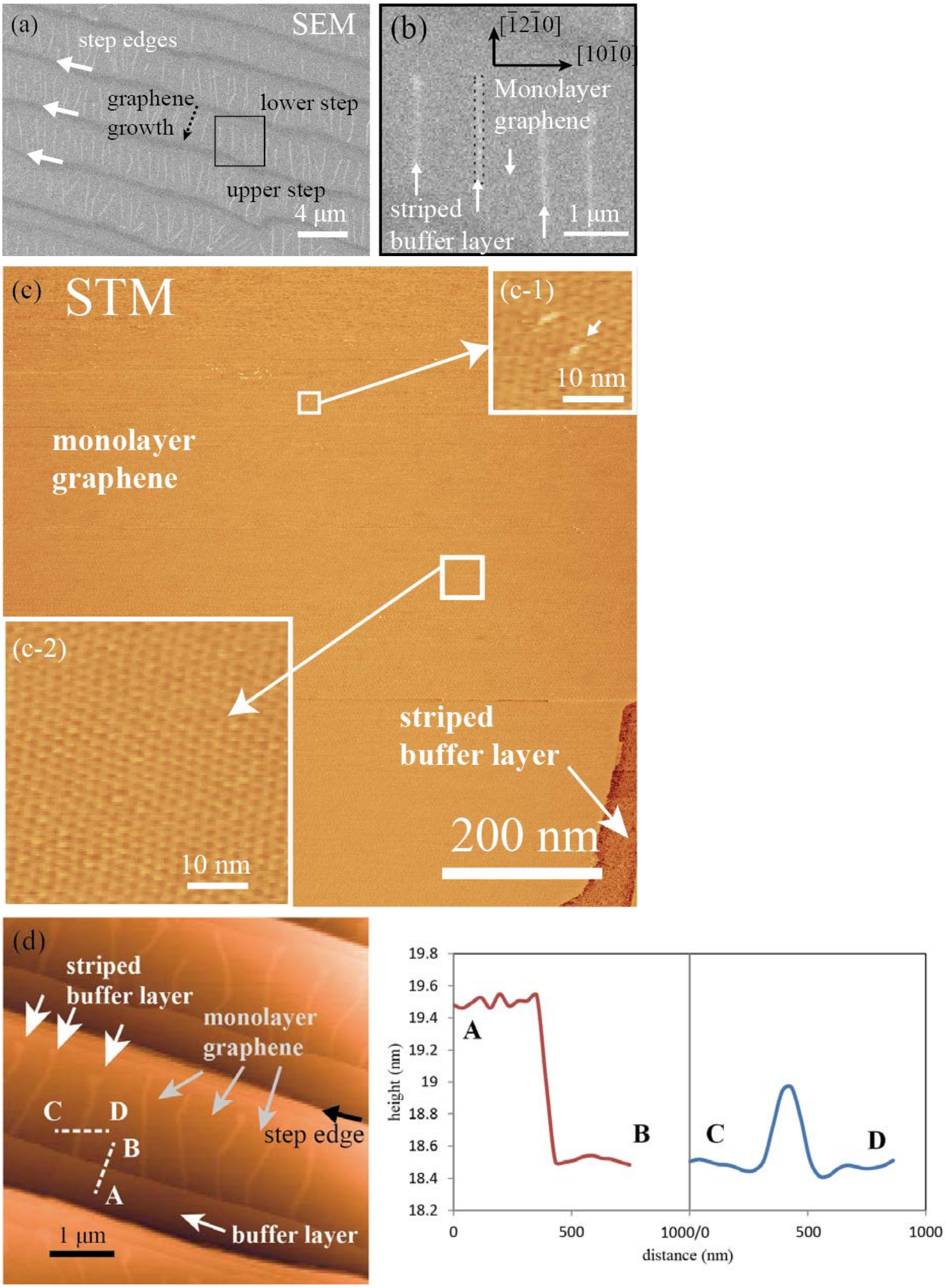

(a)
Si
Graphene
SiC
buffer layer
(b)
Si
Graphene
Pit
Pit
SiC
buffer layer

Figure 1



(a)
SEM
step edges
graphene
growth
lower step
upper step
4 µm
(b)
[$\bar{1}2\bar{1}0$]
[$10\bar{1}0$]
Monolayer
graphene
striped
buffer layer
1 µm
(c)
STM
(c-1)
10 nm
monolayer
graphene
(c-2)
10 nm
striped
buffer layer
200 nm
(d)
striped
buffer layer
monolayer
graphene
C
D
B
A
step edge
1 µm
buffer layer
19.8
19.6
19.4
19.2
19
18.8
18.6
18.4
18.2
height (nm)
A
B
C
D
0
500
1000/0
500
1000
distance (nm)

Figure 2

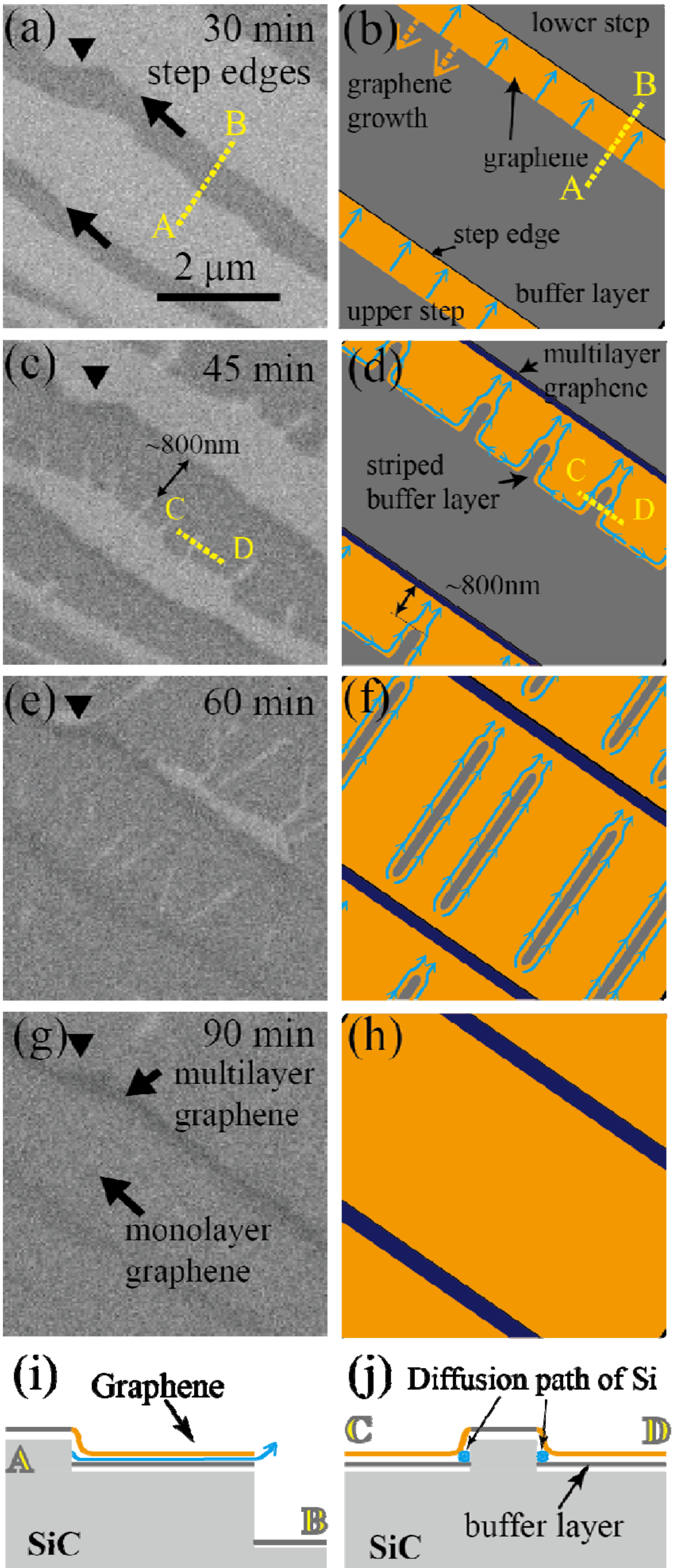

(a)
30 min
step edges
B
A
2 μm
(b)
lower step
graphene
growth
B
graphene
A
step edge
buffer layer
upper step
(c)
45 min
~800nm
C
D
(d)
multilayer
graphene
striped
buffer layer
C
D
~800nm
(e)
60 min
(f)
(g)
90 min
multilayer
graphene
monolayer
graphene
(h)
(i)
Graphene
A
B
SiC
(j)
Diffusion path of Si
C
D
buffer layer
SiC

Figure 3

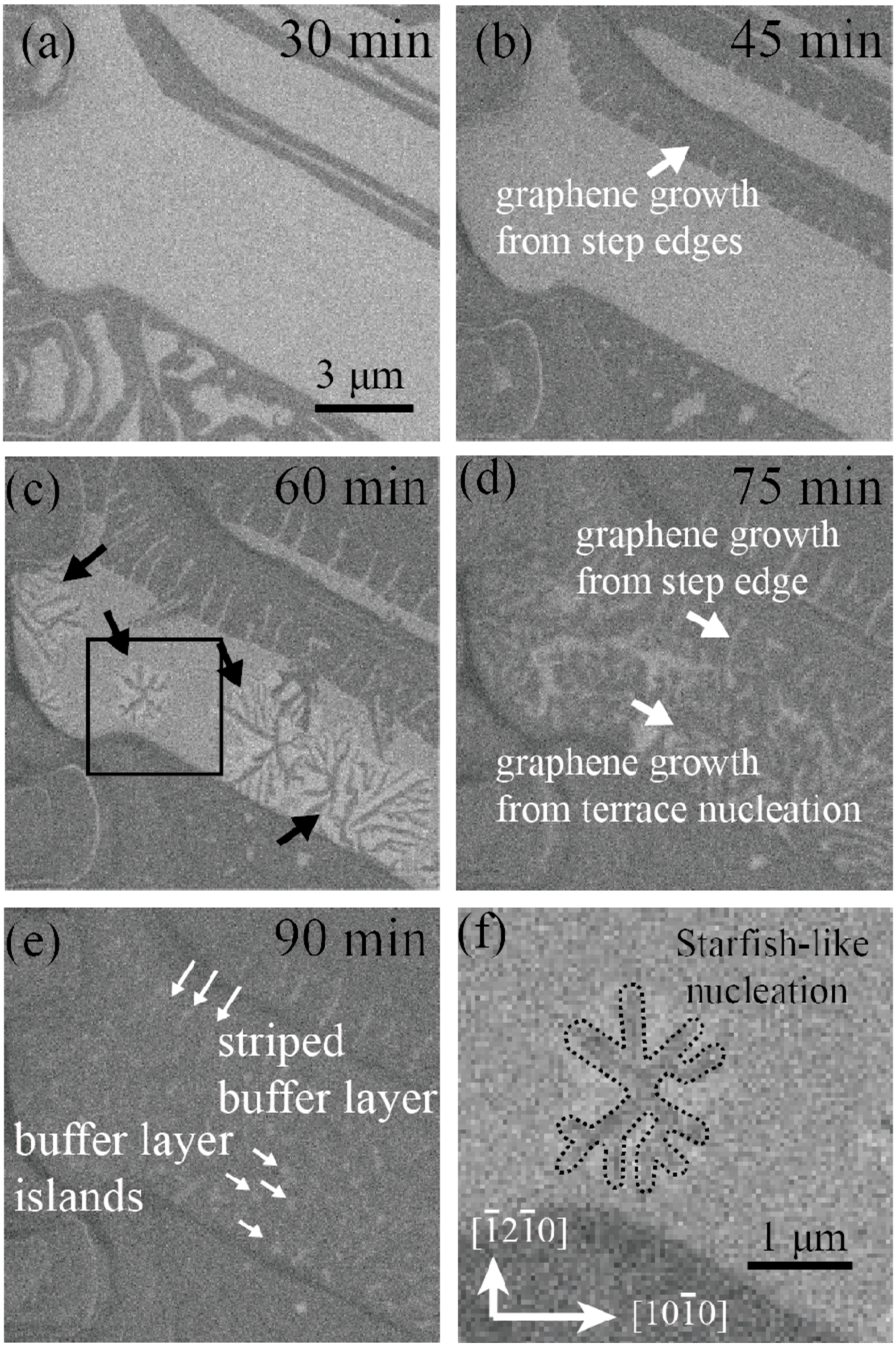

(a)
30 min
3 µm
(b)
45 min
graphene growth
from step edges
(c)
60 min
(d)
75 min
graphene growth
from step edge
graphene growth
from terrace nucleation
(e)
90 min
striped
buffer layer
buffer layer
islands
(f)
Starfish-like
nucleation
[$\bar{1}2\bar{1}0$]
1 µm
[$10\bar{1}0$]

Figure 4

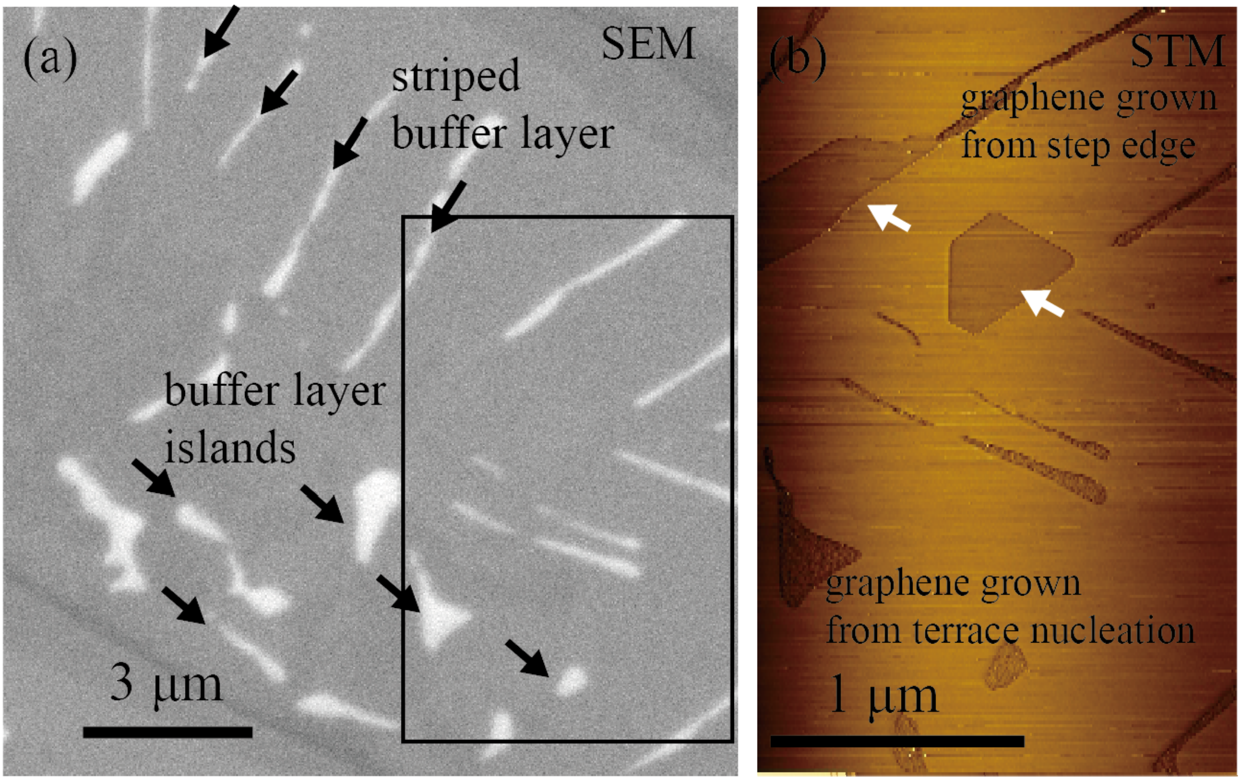

(a)
SEM
striped
buffer layer
buffer layer
islands
3 µm
(b)
STM
graphene grown
from step edge
graphene grown
from terrace nucleation
1 µm

Figure 5