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2012 Nanotechnology 23 415605

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Controllable growth of triangular hexagonal boron nitride domains on copper foils by an improved low-pressure chemical vapor deposition method

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Received 14 May 2012, in final form 2 August 2012

Published 26 September 2012

Online at stacks.iop.org/Nano/23/415605

Abstract

We demonstrate an improved low-pressure chemical vapor deposition method to fabricate hexagonal boron nitride (h-BN) domains of a few layers (one–four layers) from ammonia borane by adding a small quartz tube to stabilize the gas flow over the copper substrate and reducing the growing rate of h-BN. The h-BN grows freely and spontaneously to form triangular domains on the Cu (100) plane. The triangular domains are prone to be parallel to each other on the copper substrate. The h-BN domains grow by extending in the normal direction of the triangle and form a large thin film by joining together. Both the size and coverage rate on Cu foils are well controlled by tuning the amount of ammonia borane.

(Some figures may appear in colour only in the online journal)

1. Introduction

Hexagonal boron nitride (h-BN), an analogue of graphite, is one of the ideal dielectric materials with a wide band gap (~ 5.5 eV) [1–3] and outstanding thermal and chemical stability [4–6]. Similar to graphene, few-layered h-BN films have been fabricated by various methods, such as exfoliating h-BN powders in solution [7–11], unzipping boron nitride nanotubes [12], and by the chemical vapor deposition (CVD) method [13–16]. Up to now, CVD has been the only method to fabricate few-layered h-BN films in a large area [14, 15]. Recently, triangular h-BN domains, which are in the initial growth stage before forming large films, were observed in the CVD products [13, 16]. The growth of h-BN is significantly affected by the gas flow and metallic substrate [16]. It is still a challenge to grow large, pristine h-BN films. Controllable growth of triangular h-BN domains might lead to an understanding of the growth mechanism which would help us to fabricate high quality, pristine 2D h-BN film of large

area. Here, we control the growth of triangular h-BN domains on the copper (100) plane using ammonia borane (borazane) as precursor by an improved low-pressure CVD (LPCVD) method. We observed various stages of h-BN growth from nucleation to triangular domains, and finally to continuously large thin films. We found that the triangular h-BN domains are prone to be parallel to each other, which helps to form pristine film of large area.

2. Experimental details

Similar to the previous report [14], the growth of h-BN is carried out within a large quartz tube (50 mm in diameter) reactor mounted in a split furnace. As presented in figure 1, we modify the LPCVD setup to control the growth of h-BN by introducing a small quartz tube (20 mm in diameter) with the dead end facing to the gas flow. A piece of copper foil (99.98% pure and 25 μm thick) is placed at the end of the

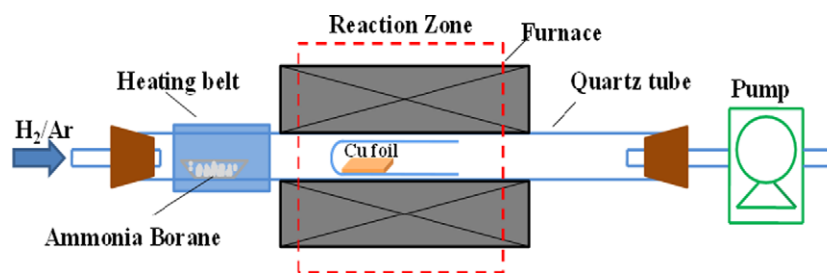


Figure 1. Schematic diagram of the LPCVD setup for h-BN fabrication.

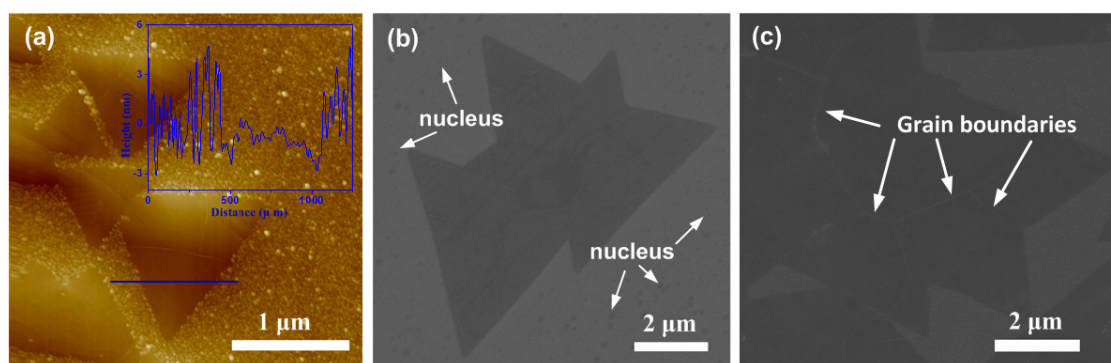


Figure 2. (a) AFM image of several parallel h-BN domains on copper. Inset is the height profile of the h-BN domains and Cu foil. (b) SEM image of several parallel h-BN domains joined together without evident grain boundaries. White arrows indicate some h-BN nuclei around the flake. (c) SEM image of a large h-BN film with evident grain boundaries.

small quartz tube. The desired amount of ammonia borane (10–200 mg) is added in a ceramic boat in front of the reactor. The reactor is directly heated to 1000 °C with the protection of Ar/H₂ (85 vol%/15 vol.%) at a low pressure of ~90 Pa. The copper foil is annealed at 1000 °C for 10 min. After that, the ammonia borane is heated slowly to 120 °C by a heating belt. The reactor is kept at 1000 °C for 2 h after the ammonia borane completely sublimates, and is then cooled down to room temperature quickly by opening the split furnace.

The h-BN domains on copper foils are directly characterized and evaluated by using a scanning electron microscope (SEM, LEO-1530), atomic force microscope (AFM, Agilent 5100), x-ray photoelectron spectroscopy (XPS, PHI Quantera), and electron backscattered diffraction (EBSD, JEOL 6500F). For transmission electron microscope (TEM, JEOL 2010) characterization, the h-BN samples are transferred to TEM grids assisted by poly(methyl methacrylate) (PMMA) as reported in graphene transfers [17]. The h-BN films coated with PMMA are dissolved in acetone for 30 min to remove the PMMA.

3. Results and discussion

Figure 2(a) shows an AFM image of several triangular h-BN domains growing on the Cu foil. It shows that the h-BN domains are in an equilateral triangle, indicating the spontaneous growth of h-BN. It clearly shows in figure 2(a) that the morphology of the Cu surface covered by h-BN is quite different from that of the uncovered surface. The exposed Cu surface is oxidized in air within a few hours,

resulting in a rough surface. The roughness of the oxidized surface measured by AFM is ~3 nm, which is of the same order as that reported in recent literature [18], while it is only ~1 nm for the Cu surface protected by h-BN. It is hard to determine the thickness of h-BN domains on the Cu substrate only by AFM measurement. It is indicated in figure 2(a) that gas molecules cannot permeate the h-BN film, thus the h-BN film can prevent the Cu from being oxidized.

Figures 2(b) and (c) show two SEM images of an h-BN flake grown from several triangular domains. It is hard to identify the grain boundary in the h-BN flake shown in figure 2(b). But, evident grain boundaries are observed in the h-BN film shown in figure 2(c). Due to the parallel triangular h-BN domains, it might form boundary-free large films when they join together. Some h-BN nuclei with a size of ~10 nm are identified in figure 2(b) (shown by arrows). The possible growth mechanism of the triangular h-BN domain is discussed below. Similar to the nucleation of graphene [19], the surface energy dominates Gibbs free energy at the beginning of h-BN nucleation, forming a round nucleus (shown by the arrows in figure 2(b)). When the volume-free energy dominates the Gibbs free energy, the h-BN nuclei grow continuously along the axes of a crystal, resulting in triangular domains, as shown in the AFM and SEM images (figures 2(a) and (b)).

Figure 3(a) shows an HRTEM image of the monolayered h-BN film. The corresponding selected area electron diffraction (SAED) pattern is shown in figure 3(b). The SAED shows the well-defined hexagonal structure of the h-BN film [20]. The h-BN film is very smooth according to the HRTEM image, showing the high quality of the h-BN film.

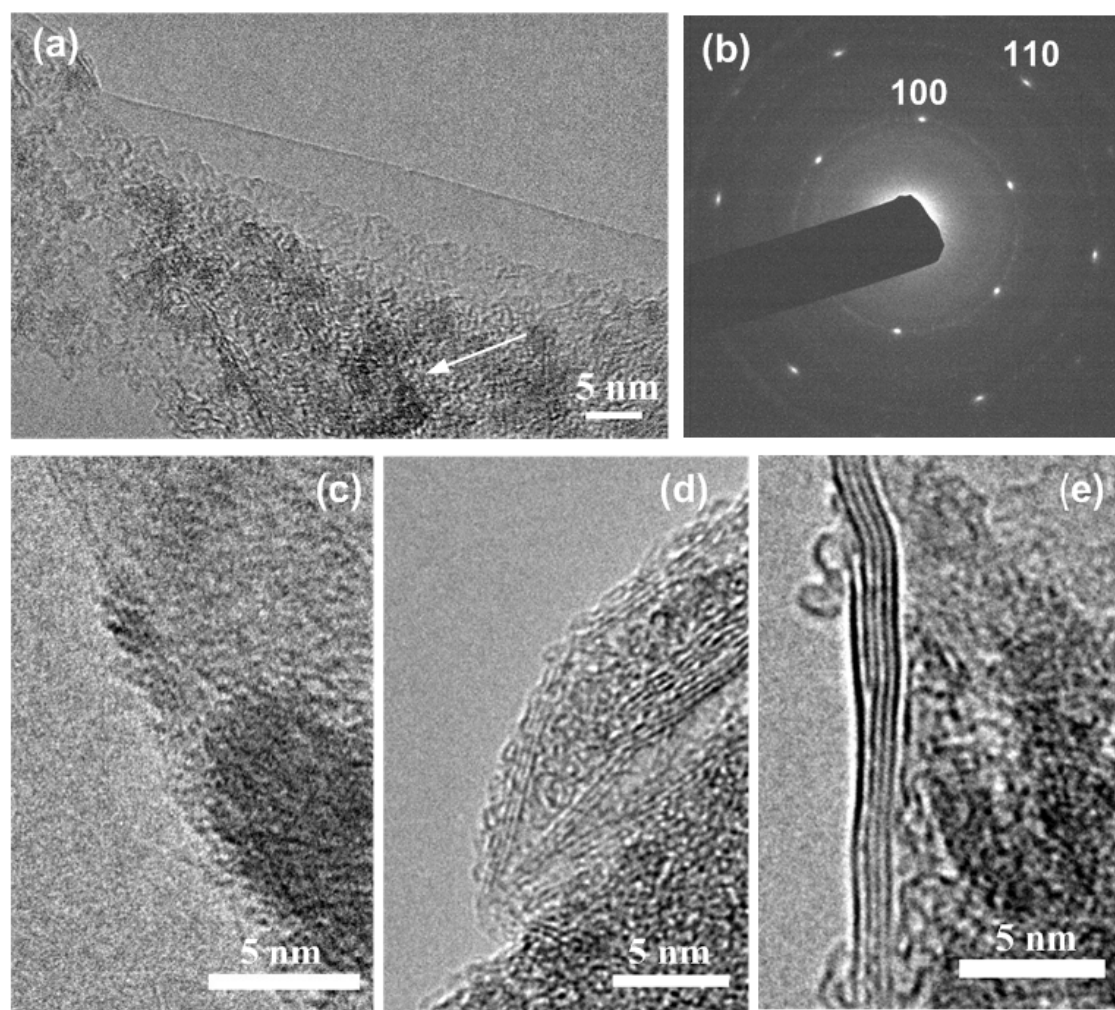


Figure 3. HRTEM images of (a) one-layered h-BN film and (b) its corresponding SAED pattern. (c) two-layered, (d) three-layered, (e) four-layered h-BN films.

Some residual PMMA is detected in samples (shown by the arrows). The h-BN films containing two–four atomic layers are also detected in the samples (see figures 3(c)–(e)).

The boron and nitride XPS spectra of the h-BN film on copper are shown in figures 4(a) and (b). The B 1s spectrum has a distinct symmetry peak at 190.1 eV, which is equal to that of the bulk h-BN [21]. The peak of the N 1s XPS spectrum is at 397.7 eV, which is close to the position of bulk h-BN (398.1 eV) [21]. The atomic ratio of boron to nitrogen calculated from the XPS spectra is 1:1, which is consistent with the stoichiometry of h-BN. It shows that our films are hexagonal boron nitride.

Generally, the growth of 2D film, such as graphene and h-BN, is affected significantly by the gas flow and substrate. The small quartz tube can stabilize and reduce the gas flow over the copper substrate, which makes it possible for the h-BN to grow slowly and freely and to form triangular domains. Figure 5(a) shows an SEM image of h-BN domains depositing on the Cu foil mounted at the dead end of the small quartz tube. It clearly shows that most of the h-BN domains are in a triangle, which indicates that the h-BN domains grow freely. We also notice that some h-BN domains are arranged

approximately in a certain direction on the copper foil, which might result from the slow gas flow over the Cu foil. The borazane decomposed to monomeric aminoborane (BH_2NH_2) and borazine (HBNH)₃ at high temperature [16]. Because the dead end of the small quartz tube faces the gas flow, the monomeric aminoborane and borazine diffuse slowly to the Cu foil. Thus, the h-BN domains grow roughly in the gas flow direction. As a comparison, we provide an SEM image of h-BN prepared by putting the Cu foil mounted outside of the small quartz tube in figure 5(b). Most of the h-BN domains have irregular shapes, resulting from the influence of gas flow.

It is very interesting that parallel triangular h-BN domains are frequently observed during the AFM and SEM examination. Ideally, the (111) plane of face centered cubic (fcc) copper is symmetry matched with the h-BN structure. Epitaxial growth of graphene and h-BN on the (111) plane of fcc metallic surfaces has been reported recently [18, 22, 23]. To elucidate the orientation of h-BN on the copper foil, EBSD was performed in SEM working at 20 kV. Figure 5(c) presents an EBSD image of the copper foil after h-BN growth. It clearly shows that Cu(100) is the surface plane of the annealed

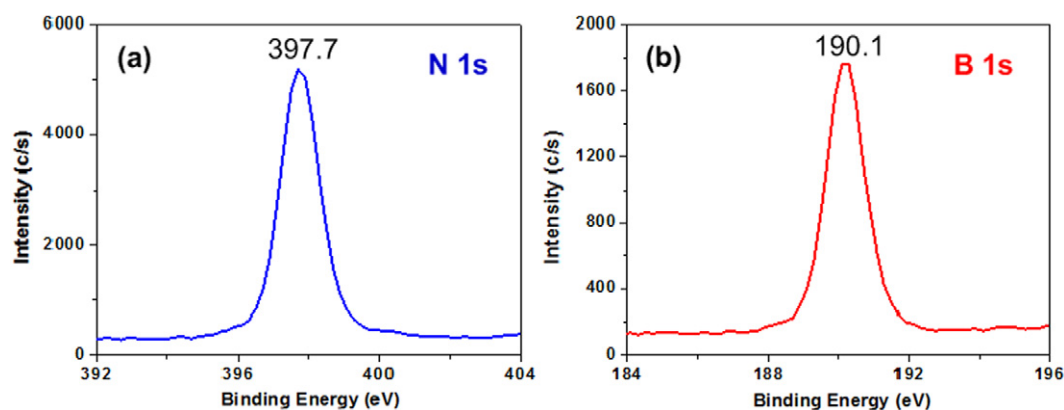


Figure 4. XPS spectra of the h-BN film: (a) N 1s spectrum, (b) B 1s spectrum.

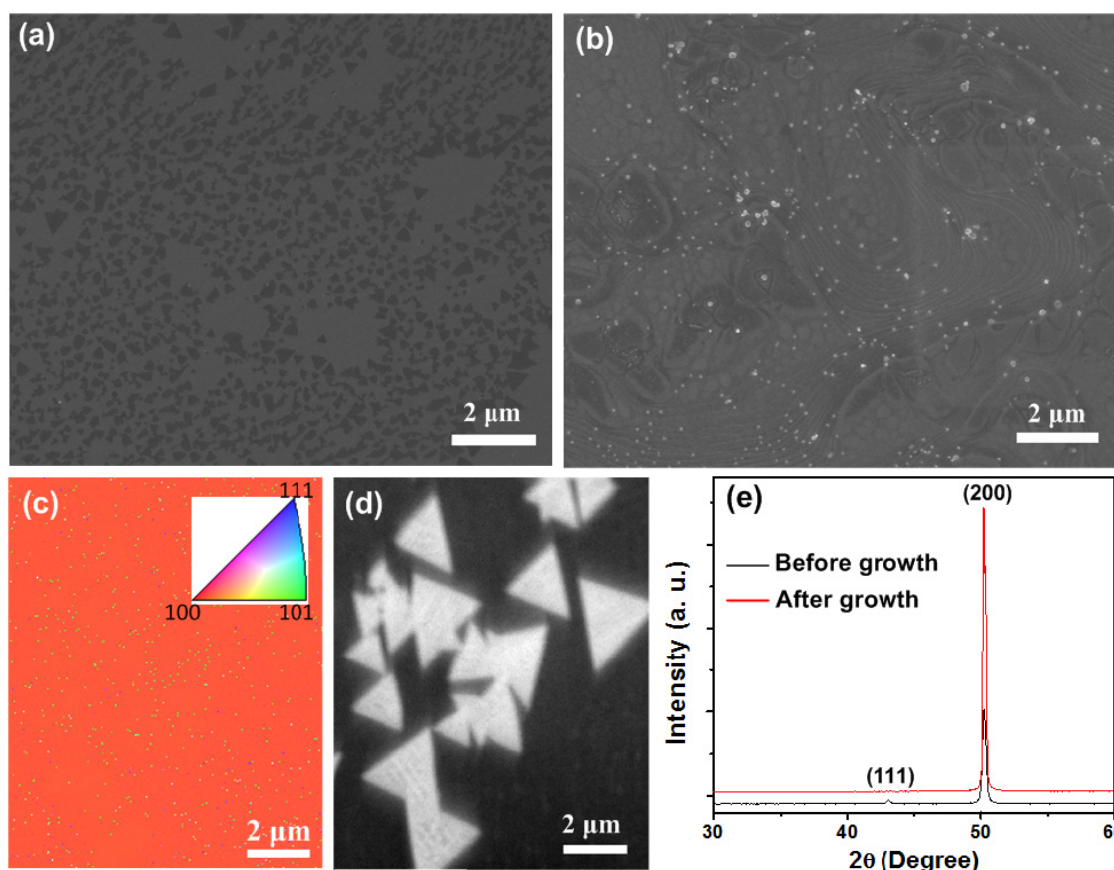


Figure 5. SEM images of the h-BN domains grown (a) inside and (b) outside of the small quartz tube. (c) EBSD image of the annealed Cu foil, showing a uniform Cu(100) plane on the Cu surface. (d) Corresponding SEM image of the h-BN domains obtained in the EBSD mode. (e) XRD profile of the Cu foil before and after h-BN growth.

copper. The (100) plane of fcc copper has four-fold symmetry, which does not match with the h-BN structure (six-fold symmetry). Thus, the parallel h-BN domains do not grow in an epitaxial way on the Cu(100) plane. The corresponding SEM image of the h-BN domains is illustrated in figure 5(d). This shows that most of the h-BN domains parallel to each other and some triangular h-BN domains growing in a rotation angle are also observed in the same area. Figure 5(d) shows that the distribution of the h-BN is not so uniform, which might result from the effect of Cu foil. Recrystallization occurs in copper

foil during the annealing at high temperature. Figure 5(e) shows XRD profiles of the copper foils before and after h-BN growth. A sharp diffraction peak at $\sim 50.2^\circ$, assigned to Cu(200) diffraction, is observed in both Cu foils. The Cu(200) peak is strengthened after h-BN growth. But the weak Cu(111) peak in the original foil disappears after annealing at 1000°C . It indicates that Cu(100) are the surface planes of the annealed Cu foils. However, future work is needed to understand the growth of the parallel triangular h-BN domains on the (100) plane of Cu foil.

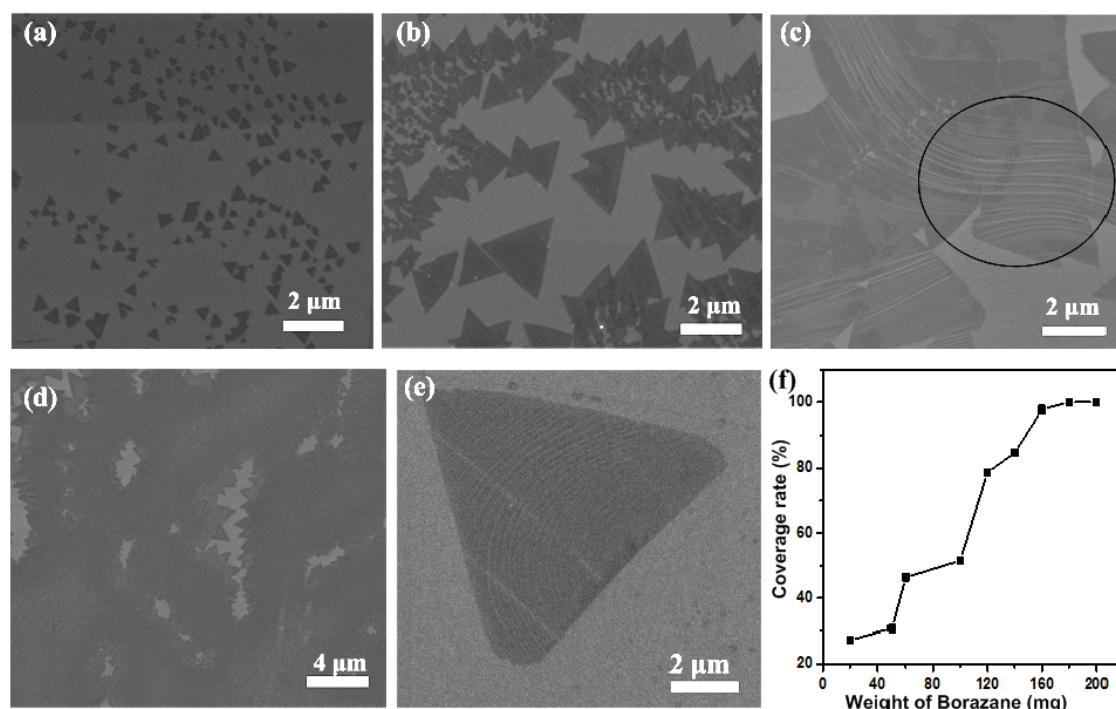


Figure 6. SEM images of h-BN domains prepared by using varying amounts of borazane, (a) 20 mg, (b) 100 mg, (c) 120 mg, and (d) 140 mg. The black circle shows the slip band of copper underneath the h-BN domains. (e) SEM image of an individual h-BN domain with size larger than 10 μm. (f) The dependence of coverage rate of h-BN domains on the weight of borazane.

We found that the size and coverage rate of h-BN domains on Cu foil are well controlled by tuning the weight of borazane if we keep the temperature of the heating belt at 120 °C (borazane sublimates at a rate of $\sim 5 \text{ mg min}^{-1}$). Figure 6 presents some SEM images, size distributions and coverage rates of the h-BN depending on the weight of borazane. By adding 20 mg borazane, the size of h-BN grains distributes mainly from 100 to 500 nm (figure 6(a)). It is the initial growth stage after nucleation. Nearly all the h-BN domains are in triangular shapes. A few small domains that join and form larger ones are also observed. The h-BN domains cover only $\sim 20\%$ of the Cu surface. When 100 mg borazane is used for h-BN growth, the coverage of h-BN domains increases to $>50\%$. The size of some individual triangular h-BN domains increases to 1.5 μm (figure 6(b)). Larger h-BN flakes forming several domains are frequently observed in the samples. With the increase of borazane to 120 mg, the h-BN domains grow larger and join to form discontinuous films (figure 6(c)). The h-BN films cover more than 80% of the Cu surface. Some copper slip bands underneath the h-BN films are identified in figure 6(c) (shown by circle). We believe the slip bands result from the quick chilling after the h-BN growth. The slip bands covered by h-BN domains are preserved, while they are eliminated by oxidation on the bare surface. It indicates that the h-BN domains contact the Cu surface tightly. When we use 140 mg borazane in the experiments, it is hard to find individual triangular h-BN domains on the Cu foils. Most of the h-BN domains assemble into larger films (figure 6(d)). The coverage of h-BN films on the copper foil increases as we add more borazane (figure 6(f)). In our conditions, it forms a

continuous h-BN film on Cu foil when $>200 \text{ mg}$ borazane is used for the h-BN growth.

There are two ways for h-BN growth: one is an individual domain extending in the normal direction of the triangular edges; the other is adjacent domains joining to form a large film. At low coverage rate of h-BN film, there are large unoccupied spaces for h-BN domains to extend freely. It is easy to observe large individual h-BN domains in the samples grown from $\sim 100 \text{ mg}$ borazane. Figure 6(e) shows an individual and pristine h-BN domain with a size of $\sim 10 \mu\text{m}$. However, at high coverage rate, the growing h-BN domains might contact with the adjacent domains and merge into a large film (figures 2(b) and (c)).

4. Conclusions

In summary, we have demonstrated here a method for controllably fabricating triangular h-BN domains of a few layers (one–four layers) on the Cu(100) plane by using a small quartz tube to reduce the gas flow. Due to the stabilization of gas flow over the copper foil, the h-BN grows freely and forms triangular domains. The h-BN domains grow by extending in the normal direction of the triangular edges. The adjacent domains join together and form a large area film. The triangular h-BN domains are prone to be parallel to each other, which helps to form boundary-free h-BN films. The size and coverage rate of the h-BN domains on Cu foil are well controlled by tuning the amount of borazane.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51172122), the Foundation for the Author of a National Excellent Doctoral Dissertation (2007B37), and the Tsinghua University Initiative Scientific Research Program (20111080939).

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