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A comprehensive investigation on CVD growth thermokinetics of h-BN white graphene

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Abstract

As an isomorph of graphene, monolayer hexagonal boron nitride (h-BN), so-called white graphene, has been in the spotlight of two-dimensional materials due to its outstanding properties. However, the growth of large and uniform white graphene monocrystalline with low density of defects is still a great challenge. Here, we present a comprehensive investigation on the growth thermokinetics of white graphene monocrystalline domains via atmospheric pressure chemical vapor deposition with the solid ammonia borane as precursors, which will be more suitable for future industrial production due to the handy process and precursor. The single domain size, coverage on substrate, and thickness of white graphene were taken as targeted parameters of products. And then, their dependences on the flow rate of carrier gas, heating temperature of ammonia borane, growth temperature and time were studied in details. Finally, after optimizing the above conditions, both white graphene monocrystalline domains as large as 80 μm² and polycrystalline ultrathin film with coverage ratio of 95%–100% can be achieved facilely without using vacuum technique. Such white graphene products would be of great significance for the tunnel barrier for the tunneling transistor and the dielectric layers for nanocapacitor with the graphene based heterostructures.

1. Introduction

As the structure analog of graphene, monolayer hexagonal boron nitride (h-BN), so-called ‘white graphene’ [1], has caught enormous attentions in past few years owing to its unique structure, various outstanding properties, and potential applications in the electronics [2–4].

h-BN is comprised of alternating boron and nitrogen atoms in the honeycomb arrangement, with the strong sp² B-N hybridization in plane and the weak van de Waals force between the adjacent layers. Due to the atomic-scale smooth surface with free dangling bonds, charge traps, as well as the low lattice mismatch with graphene (1.7%), h-BN has been a promising substrate for graphene related application, which can significantly promote the carrier mobility of graphene [5]. In contrast to graphene (zero band gap), h-BN has a large direct band gap from 5.4 to 6.0 eV [6], rendering it an ideal candidate for insulator material and dielectric layer in field effect transistors [7]. White graphene can also hybridize with graphene to tune the electronic structure and the electronic properties of devices [8, 9]. In addition, h-BN film shows high mechanical strength, extraordinary thermal conductivity, superior stability, good dielectric property, and excellent optical property, which make the h-BN a promising material in the industrial applications, especially for electronic and optoelectronic devices [2, 8–12]. However, for the practical application, it requires a large area and high-quality white graphene with large domain size and perfect interfacial properties with the heterojunction. Various methods have been developed to synthesize h-BN, such as micro-mechanical cleavage [13], liquid phase exfoliation [14], unwrapping BN nanotube [1], and chemical
vapor deposition (CVD) [15–32]. Among them, only the CVD approach has been a feasible route to achieve large and high quality monolayer or few layers h-BN film for practical application. Significant effort has been dedicated to synthesize large area h-BN films by a low pressure CVD (LP CVD) or atmospheric pressure (APCVD) method on various substrate, such as Ni [17], Cu [20], Pt [16, 19, 22] foils or Si/SiO₂ [15]. However, the size of single-crystal white graphene domains was limited to several micrometers [16, 20]. And the obtained large area h-BN film is a polycrystalline structure with a high density of domain/grain boundaries, which can hinder the transport of charge carriers at the interface and affect the interfacial properties of the heterojunction with graphene [26, 33]. Therefore, enlarging the size of the single-crystal h-BN grain domain remains as one of the greatest challenges for the synthesis of white graphene.

To produce large area single-crystal white graphene domain with a CVD process, a common strategy is to reduce the nucleation density by minimize defect density on copper surface through various pretreatments [27, 34]. For example, Khan et al [18] prepared the high quality micro-sized single crystalline h-BN on the melted copper substrate. Using an electropolished Cu foil, Tay et al [24] obtained a 35 μm² large single-crystal h-BN hexagons under APCVD conditions. Through a long duration (6 h) annealing of copper foils, Wang et al [26] improved the quality of Cu surface to reduce the nucleation density of h-BN and synthesized 10–20 μm, single-crystal h-BN domains. During the h-BN growth, effects of H₂ etching have also been used to reduce the new growth nucleation around the large domains. The single crystalline h-BN domains can grow up to 50–100 μm [27]. Recently, by regulating the atom ratio of Cu–Ni alloy substrate, Lu et al [21] obtained the largest single-crystal h-BN, the size is up to 7500 μm², which is two order of magnitude greater than the traditional copper substrate. However, these mentioned methods are based on the treated copper substrates, which is typically highly expensive and the processes are complicated. In fact, for the growth of large scale single crystal white graphene domains, one must balance the growth thermokinetics during the processing. However, the CVD growth thermokinetics and the growth mechanism of h-BN film are still not clear so far. It hinders the preparation of high-quality h-BN, as well as the industrial application in the future.

Here, we present a comprehensive investigation of APCVD growth thermokinetics of white graphene. We study the dependences on the flow rate of carrier gas, heating temperature of ammonia borane (AB), growth temperature and time in details aiming at achieving the large single-crystalline h-BN domain and high film coverage ratio on the substrate. Utilizing the optimized growth conditions, we obtained the single-crystal of white graphene domain with size up to ~80 μm² and the coverage ratio up to 95%–100% on a Cu substrate (size: 1.5 × 1 cm²). Based on the systematically investigation on the growth of white graphene, an adsorption–nucleation-growth models are used to analyze the growth mechanism of white graphene.

2. Experimental section

2.1. Synthesis of h-BN on Cu foil

The growth of BN film was carried out in the split tube furnace as shown in figure 1(a). We use the 25 μm thick copper foil as the substrate and the catalyst which is purchased from Alfa Aesar. Ammonia borane (H₃NBH₃), solid at room temperature with B and N atoms in 1:1 stoichiometric ratio, was used as precursor and was placed in a ceramic holder and kept 60 cm away from Cu foil substrate. Before deposition, Cu foil was dipped into dilute hydrochloric acid and has rinsed in DI water for three times. After that, Cu was dipped in ethanol ultrasonic cleaning for 5 min Finally, it was dried by nitrogen flow. Then Cu foil was put into furnace and heated to the temperature of 1000 °C and annealed for 30 min in Ar/H₂ atmosphere. At the growth temperature, we heat the ammonia borane which was placed in a ceramic holder within the quartz tube with a flexible heating belt. Then, we adjust the flow rate, reaction temperature, reaction time, precursor temperature, and substrate position to control the domain size and film thickness.

2.2. Transfer process

The as-grown h-BN film was transferred onto SiO₂/Si wafer. The dissolved PMMA in the acetone solution was first coated on the Cu substrate at 3000 rpm for 30 s, then FeCl₃ solution was used to etch away the Cu substrate. The free standing PMMA coated h-BN was then rinsed in DI water several times and extracted onto the target substrate. The target substrate was heated to 70 °C and has kept for 60 min to make a strong adhesion between h-BN and the substrate. Finally, the sample was immersed in hot acetone for several hours to remove the PMMA upholder.

2.3. Characterization

The morphology and thickness of h-BN under the different conditions was investigated by field emission scanning electron microscopy (SEM; Quanta 250) and atomic force microscopy (AFM; Dienson Icon). The vibration modes and unique signature of h-BN film were analyzed by the Raman spectroscopy (Raman; HJY Aramus) with 532 nm excitation laser wavelength. The specific binding energies of boron and nitrogen atoms were detected by the x-ray photoelectron spectroscopy (XPS; ARL perform). We used the UV-visible spectrophotometer (UV-3600) to measure the absorption spectrum and calculated the optical band gap (OOG) of h-BN, and high resolution transmission electron microscopy (HRTEM; FEI Tecnai 20) was applied to verify the crystal structure and the quality of
h-BN film. Optical microscopy (Olympus BX51) also was utilized to have a quick observation at the morphology of as-grown h-BN film.

3. Results and discussion

3.1. Domain dependences on growth conditions
To explore the growth mechanism of white graphene domain, as well as the thermokinetics of the CVD process, a systematic study of the growth process with regulating different parameters on the morphology of white graphene was performed. In this section, we discussed the effects of substrate position, growth temperature, heating temperature of AB, flow rate as well as the growth time on the microstructure of white graphene.

3.1.1. Substrate position dependence
Substrate position plays a vital role for obtaining homogeneous two-dimensional materials [35]. Both the morphology and thickness of the as-grown film vary with the substrate position even if all the other parameters are the same. To study this position dependence, the 8 cm long Cu foil is divided into four 2 cm long regions A, B, C, and D as shown in the figure 1(a).

As depicted in figures 1(b)–(f), the SEM images of the obtained h-BN at different regions confirmed the importance of the substrate position for controlling the film-growth and coverage. The density of h-BN domain and film coverage gradually increased from region A to region D. The density and coverage of h-BN in region A is ∼15% while the region C is mostly covered and the density is as large as ∼80%. Moreover, the area of h-BN is also getting larger from ∼2 μm² to ∼15 μm². The domain size in region C is about seven times larger than that in region A. This trend is consistent with other reports on the growth of graphene and h-BN with CVD system [25, 35].

Considering the above CVD process and the dehydrogenation mechanism of borazine, the phenomenon we observed may be explained as follows. Following the decomposition of ammonia borane, the cold gas including borazine downstream with the carrier gas along the quartz tube. As the transportation proceeds along the tube, the temperature of borazine molecule rises. According to the Arrhenius equation (formula (1)), rising temperature expedites the reaction in an exponential fashion

\[ K = A \exp(-E_a/RT). \]  

Where \( K \) is rate constant of action, \( A \) is a constant, \( T \) is temperature, \( E_a \) is the activation energy, and \( R \) is the constant of Moore gas.

When borazine molecule entered the reaction region A, the temperature of the molecule is not sufficient high leading to a low reaction rate. However,
when borazine molecules are continuously transported by the carrier gas, the temperature of borazine molecule increases. Therefore, at region C, molecules collide, diffuse and react at a much higher rate, resulting in a much faster domain growth. Furthermore, borazine molecules can polymerize in the gas phase. The macromolecule dehydrogenized directly which initiates the nucleation process. Based on the above analyses, the speed of nucleation and growth at downstream position is faster than that in upstream position (figure 1). Thus, in order to achieve high quality and homogenous h-BN film, the control of surface reaction and gas equilibrium is crucial and it requires a suitable flow rate and a precisely controlled temperature gradient.

3.1.2. Growth time dependence

The morphologies and thickness of h-BN film (such as monolayer, bilayer, and few layer h-BN films) can be regulated by varying the growth time. As the time increased, the domain size and the film coverage also enlarged. Figure 2 shows SEM images of the as-grown h-BN domains on Cu substrate at region C with different growth time of 10, 20, 30, and 60 min, respectively. As shown in figure 2(a), with short growth time (10 min), the h-BN domains are isolated small triangles. When the growth time exceeds 20 min, the domains start to overlap (figure 2(b)). With even longer growth time (figures 2(c) and S2(a)), the films become continuous and finally cover Cu surface completely. The film coverage and domain size, as well as the thickness of the films (figures 2(d) and S2(b)), increased with the extension of growth time. Thus, we can obtain the h-BN film with different coverage and domain sizes by simply controlling the growth time.

The thickness variation of the h-BN domain indicates that the h-BN film growth on Cu substrate with APCVD is not self-limited, which is different from the self-limited growth of graphene due to the different growth mechanism [36]. The solution-precipitation process plays an important role in the growth of graphene. The low-solubility of carbon atoms in Cu substrate and the decreased catalytic activity of Cu make it easy to obtain the monolayer graphene. However, different from graphene, the single domain of h-BN is not always monolayer suggesting that the growth of h-BN may follow the combination of layer-by-layer growth and island growth model (Stranski–Krastanov growth) [20]. Following this growth model, with longer growth time, one can obtain the large area multilayer h-BN films.

3.1.3. Growth temperature dependence

It is well known that the control of growth temperature is widely used for synthesizing the graphene with various morphologies [35]. Previous results showed that the changing of the annealing temperature and growth temperature will cause significant differences in thickness, grain size, growth rate, and shapes of graphene [37]. In our experiment, three different temperatures: 950 °C, 1000 °C and 1075 °C were employed as growth temperature. The SEM images shown in figure 3 demonstrate the variations of domain size and density on the Cu surface. With the temperature increasing from 950 °C to 1000 °C, the size of each individual domain is enlarged by about three times, meanwhile, the shape of h-BN tended to

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**Figure 2.** SEM images of the as-grown h-BN film using 15 mg ammonia borane probed in position region C on Cu with different growth time. (a) 10 min (b) 20 min (c) 30 min (d) The variation of film coverage and domain size on the dependence of the growth time.
change from triangle to hexagon. Theoretical calculation predicates that the growth of h-BN typically results in a triangle with N-terminated edge due to the high energy of B-terminated edge \[20, 23, 28, 38\]. However, in our experiments, several kinds of shapes such as conventional triangle, hexagon, and asymmetric diamond-shape were observed during the growth process of h-BN. It agreed with the theoretical calculation of Liu \textit{et al} which predicted that the shape of h-BN may evolve between triangle and hexagon under different growth conditions \[38\]. Recently, Tay \textit{et al} has firstly synthesized the h-BN hexagons on electro-polished Cu substrate and study the effects of Cu surface on the h-BN shape \[24\]. With continuous increasing of temperature to 1075 °C, the domain size experiences a drastic increase to an average size of \(\sim 75 \mu m^2\). From the analysis of three typical growth temperatures, we found that the growth temperature not only influence the grain size, but also the domain shape. Therefore, by simply controlling the growth temperature, we can obtain the h-BN grain with different shapes and sizes.

We also found that the pretreatment of Cu is necessary in the synthesis of high quality h-BN. The figure S3(a) shows the h-BN grown on the Cu without any pretreatment. The nucleation density is high with plentiful heterogeneous sites. The detail drawing of domains is showed in the figure S3(b). As indicated by the red arrows, there are many nucleation sites existing at the small region which lead to the abundant grain boundaries in the as-grown h-BN film. In addition, the yellow arrows point at many little domains mingled in the large domains. The inhomogeneous growth may result in the non-uniform thicknesses in the adjacent region, which can hinder the transferred process and further leads to the poor quality of h-BN film \[26\].

The increasing of temperature from 950 °C to 1075 °C may change the surface morphology of Cu surface. The main rolling streaks, impurities, and CuO or CuO\(_2\) can be further eliminated. The tempestuous and sufficient recrystallization of Cu substrate at higher temperature will result in a smoother surface with larger grain and lower density of defects. The larger crystal grain of Cu in higher temperature is very important for synthesizing the large single crystal with few defects including graphene and h-BN. With higher growth temperature, the dehydrogenation is more drastic, which leads to the faster growth of the h-BN, as well as film coverage from \(~20\%\) to \(~80\%\).

The growth rate of h-BN and catalytic activity of Cu substrate dramatically increased with the temperature, which consequently leads to the more acutely dehydrogenation of the borazine molecule. The species with high activity may tend to form h-BN with hexagon shapes in the Cu surface due to the free energy \[28, 38\].

### 3.1.4. Flow rate dependence
The effects of the carrier gas flow rate on the morphologies of h-BN are also studied. Three types of flow rate 75, 150, and 300 sccm are employed in our work. In the precious studies of graphene, the flow rate was used as an important parameter to tune the nucleation density and morphology of graphene \[34\].

There is a significant effect on the domain density of h-BN domains by the flow rate (figures 4(a)–(c)). With the flow rate decreased from 300 to 75 sccm, the
density of nucleation decreased clearly, but the size of the domain almost unchanged. Under the large flow rate circumstance (300 sccm), the domains overlapped with each other (figure 4(c)). With small flow rate (100 sccm), the domains become isolated (figure 4(a)) while no obvious changes in domain size are observed after tuning on the flow rates. In addition, when the flow rate is lower than a critical value, there is no nucleation observed on the Cu substrate in our experiment. Figure 4(d) shows the schematic diagram of the borazine molecules from low temperature to high temperature region. The borazine molecules may decompose or polymerize during the transporting, as illustrated by process 1 in figure 4(d). With the increasing of flow rate, greater amount of precursor can be supplied for the reaction leading to the larger coverage of h-BN film and the increasing nucleation sites [37]. Moreover, the lower the gas flow is, the smaller amount of borazine that can reach the surface of Cu, and there is less formed nucleation for the growth of h-BN. Thus, a higher critical value of flow rate is necessary which will introduce more decomposition of precursor to Cu surface.

3.1.5. AB heating temperature dependence
Solid precursor with two separated heating regions was widely used in the synthesis of h-BN because of the convenience and low-cost of reaction equipment. But due to the poor control of the concentration, it is hard to obtain high quality films with APCVD method.

The heating temperature of AB which influences the concentration of borazine will be discussed in this part. Several groups have conducted studies on the heating temperature of precursors [20, 25]. Here, we employed the temperatures varied from 80 °C to 100 °C with a step of 5 °C, as shown in figures 5(a)–(e). Interestingly, when temperature is lower than 60 °C, there is no h-BN domain found on the Cu substrate. Owing to the property of AB, there may be no decomposition reaction or the concentration of generated borazine is insufficient for nucleation when temperature is lower than 60 °C. The film coverage, thickness of domain, and nucleation sites increased with the temperature increasing. As shown in figures 5(a) and (d), the domain size increased by about 5 times when the temperature is varied from 80 °C to 90 °C.

However, with the increasing nucleation density, the domain size shows a maximum value at the 90 °C, the curves in figure 5(f) indicates the relationships of domain size and film coverage versus temperature. Here we define the coverage rate, $\nu_{\text{cov}}$, as the increased of the h-BN coverage (h-BN area $A_{\text{BN}}$, Cu surface area in the field of vision, $A_{\text{Cu}}$) within the unit time showed as formulas (2) and (3)

$$
\nu_{\text{cov}} = \frac{dA_{\text{BN}}}{A_{\text{Cu}}dt} \quad (2)
$$

$$
\nu_{\text{domain}} = \frac{\nu_{\text{cov}}}{n} \quad (3)
$$

The increasing of concentration will expedite the growth rate (the increase of $\nu_{\text{cov}}$) of h-BN, meanwhile, the quantity of nucleation sites ($n$) increased due to the violent polymerization and dehydrogenation. Hence, the coverage ($A_{\text{BN}}$) increased with time. As illustrated by formula (3), with the temperature increased, the increasing $n$ has a great influence on the $\nu_{\text{domain}}$ which reduce the growth rate of single h-BN domain (the decrease of $V_{\text{domain}}$).
3.2. Characterizations of the representative h-BN films

The h-BN domain obtained in the LPCVD system is not always in the triangular shape (figure S1) \[20\]. Theoretically, comparing to the higher energy boron-terminated edge, the lower energy nitrogen-terminated edge makes the triangular shape energetically favorable \[28, 38\]. In fact, the different shapes of independent as-grown h-BN domains have been reported, such as hexagon \[24\], diamond shapes \[20\], and other irregular forms \[23\]. Moreover, the shape of h-BN in our experiment is not always the same due to the varying parameters and the surface condition of Cu.

According to our systematical investigation of white graphene growth, we chose an optimized growth condition to synthesize white graphene (time: 60 min, temperature: 1050 °C, flow rate: 200 sccm, temperature of AB: 95 °C), and a large area h-BN film with the size of $1.5 \times 1.0 \text{ cm}^2$ on Cu foil was obtained.

Figure 6(a) presents the h-BN film transferred onto 300 nm SiO$_2$/Si wafer with the size about $1.5 \times 1.0 \text{ cm}^2$, the light-blue region is the h-BN film. Due to small optical contrast with SiO$_2$/Si wafer, it is hard to observe thin h-BN film. With the detection of SEM (figure 6(b)), we found the as-grown h-BN films possess high quality with large area and less impurities.

The large, high quality and continuous film normally comprised of the h-BN domain with regular shape. By controlling the parameters (time: 20 min, temperature: 1075 °C, flow rate: 200 sccm, temperature of AB: 90 °C), we obtained the hexagonal shaped h-BN domain (figures 6(c) and S4). The size of single crystal domain is about 20 μm with the area of 80 μm$^2$, which is larger than those without substrate treatments \[20\]. The single domain was analyzed by the HRTEM, and the results presented in figures 6(d) and (e), which presents a monolayer h-BN. The distance between the adjacent protuberant atoms is 0.25 nm, consistent with the $[100]$ BN lattice. The observed the single hexagonal dot electron diffraction patterns in the FET image indicates the hexagonal structure of h-BN film with high quality, as shown in the inset image of figure 6(e).

Figure 6(f) displays the EELS spectrum of h-BN film, which is used to determine the stoichiometric ratio of boron and nitrogen atoms, as well as the chemical states of h-BN film. There are two distinct

![Figure 5](image-url)
absorbance features in the spectrum which start from 190 and 402 eV, corresponding to the K-shell ionization edges of boron (B–K) and nitrogen (N–K) of h-BN, respectively. The π* peaks and the σ* bands of the B–K and N–K edges are typical of the sp²-bonded layered h-BN. The stoichiometric ratio of adjacent dots calculated is close to 1.0 (figure 6(f)).

The thickness of single domain is about 1 nm, which is consistent with experimental results of monolayer h-BN that transferred onto SiO₂/Si substrate (figures 6(g) and (h)). The h-BN film was further characterized by Raman spectrum to analyze the lattice vibration mode of film, the Raman spectrum shows in figure 6(c). As we observed, Raman peak is located at 1370 cm⁻¹, corresponds to the reported F₂g vibration mode of the h-BN film [16, 19], and indicating the high quality of the obtained h-BN film in our experiment. XPS measurement is also adopted to characterize the elements of the as-grown h-BN film. Figure S5(a) shows the XPS spectra of h-BN film on the Cu substrate, and the binding energies of boron 1s and nitrogen 1s showed in the figures S5(b) and (c). The measured binding energies of B 1s and N 1s are 190.1 eV and 397.8 eV, respectively. The calculated stoichiometry of boron and nitrogen was 1:1, which are consistent with the EELS spectrum and previous studies [19].

The h-BN films were farther transferred onto the quartz substrate to measure the absorption property and OBG. The h-BN thin film is transparent in the light from visible to infra-red wavelength, and the single sharp absorption peak obtained is around 203 nm in our observation (figure S6(a)). The OBG derived is 5.97 eV in our experiment, closing to the theoretical calculation of thin h-BN film [39] (figure S6(b)). However, the typical OBG of bulk h-BN is 5.2–5.4 eV [6]. The interlayer interaction plays a critical role in the electronic band gap of h-BN which leads to the
increased OBG with the decreasing thickness of h-BN film. The large OBG of h-BN indicates that h-BN can be used as a deep ultraviolet material and a superior insulating material in the future nano-electronic device.

3.3. Growth process of white graphene via APCVD

Ammonia borane (AB), which is a stable and temperature sensitive material, was used as a precursor to synthesize the h-BN film on the polycrystalline Cu foil in our experiment. When reaching its decomposition temperature, AB dissociates into hydrogen (H₂), borazine (B₃H₆N₃; gas), and polyiminoborane ([BH₂NH₂]ₙ; solid) [19, 20, 40]. The borazine gas is transported by the Ar/H₂ carrier gas to the react region, providing the main building blocks for h-BN growth.

After systematically investigating the effects of process conditions on the nucleation density and domain size of h-BN, we introduced adsorption–nucleation-growth models to analyze the growth mechanism of white graphene, which was borrowed from the synthesis of graphene. The CVD process of white graphene is more complicated compared with graphene due to a balance of B and N atoms during the growing. Borazine molecule, with a ring structure composed of alternant boron and nitrogen atoms producing from AB, is selecting as a precursor to prepare h-BN films. The main CVD thermokinetics process and reaction of borazine molecules are showed in the figure 7. Via the vapor transporting by Ar/H₂ gas, the borazine molecules generated by the decomposition of AB, flow from low temperature (about 90 °C) to high temperature (1050 °C). As illustrated in the figure 7, generally, there are several steps: ① borazine molecules transport to the reaction region and are adsorbed on the copper surface, ② the borazine molecules diffuse on the surface while being dehydrogenated, ③ the dehydrogenated active species diffuse and combine to form thin film. The catalysis-dehydrogenation-nucleation process is pivotal to the CVD growth which is affected by various parameters including the growth temperature. Moreover, borazine molecules can polymerize in the gas phase as shown in figure 7 process ④ and ⑤. Compared to the upstream molecules, the downstream molecules have been carried over longer distances and have more time to be elevated to a higher temperature. Thus, the downstream molecules are prone to form polyborazilelene, and then the macro-molecule dehydrogenized providing the seeds for nucleation and growth.

4. Conclusion

In summary, we successfully prepared the high quality h-BN film by a systematic study of the thermokinetics of APCVD. The factors such as substrate position, precursor heating temperature, flow rate, growth temperature and the growth time, which have significant effects on the kinetics and thermodynamics of h-BN film growth, are well discussed in the paper. The adsorption–nucleation-growth mechanism is introduced to explain the growth process of white graphene. With the optimized growth condition, we obtained single-crystalline domains with the mono-layer and the area of 80 μm² and a polycrystalline ultrathin film with coverage ratio of 95%–100%. The ultrathin and large area h-BN films make it an ideal candidate for future applications in graphene based filed effect transistor.

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