Synthesis of Patched or Stacked Graphene and hBN Flakes: A Route to Hybrid Structure Discovery

Soo Min Kim, Allen Hsu, P. T. Araujo, Yi-Hsien Lee, Tomás Palacios, Mildred Dresselhaus, Juan-Carlos Idrobo, Ki Kang Kim, and Jing Kong

†Department of Electrical Engineering and Computer Sciences and ‡Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
§Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
∥Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), Jeollabuk-Do, 565-902, Republic of Korea
⊥Department of Energy and Materials Engineering, Dongguk University-Seoul, 100-715, Republic of Korea

Supporting Information

ABSTRACT: Two-dimensional (2D) materials such as graphene and hexagonal boron nitride (hBN) have attracted significant attention due to their remarkable properties. Numerous interesting graphene/hBN hybrid structures have been proposed but their implementation has been very limited. In this work, the synthesis of patched structures through consecutive chemical vapor deposition (CVD) on the same substrate was investigated. Both in-plane junctions and stacked layers were obtained. For stacked layers, depending on the synthesis sequence, in one case turbostratic stacking with random rotations were obtained. In another, “AA-like”, slightly twisted stacking between graphene and hBN was observed with lattice orientation misalignment consistently to be <1°. Raman characterizations not only confirmed that hBN is a superior substrate but also revealed for the first time that a graphene edge with hBN passivation displays reduced D band intensity compared to an open edge. These studies pave the way for the proposed well-ordered graphene/hBN structures and outline exciting future directions for hybrid 2D materials.

KEYWORDS: Boron nitride, graphene, hybrid, chemical vapor deposition, heterostructure

Graphene has attracted a lot of attention due to its remarkable electronic and optical properties.1–4 Its counterpart, hexagonal Boron Nitride (hBN), has a very similar structure and also many attractive properties, such as comparably high in-plane mechanical strength, thermal conductivity, and excellent chemical inertness even better than graphene.5–9 It has been shown that hBN is a large bandgap semiconductor (5.97 eV)10,11 and can serve as a superior substrate for graphene devices: the on-substrate mobilities of graphene on exfoliated hBN is comparable to that of suspended graphene.12 As a consequence, graphene and hBN hybrid systems have great potential as the channel and the substrate/gate dielectric materials for next generation electronic devices.13,14

There have been many interesting predictions about the properties of hybrid graphene/hBN structures. For an in-plane structure (Figure 1a is one example), it was expected that hBN domains in graphene can open a bandgap depending upon their concentrations (0.4 eV bandgap for ~0.1 hBN concentration).15 It has also been suggested that graphene nanoflakes (GNFs) embedded in an hBN layer will act as quantum dots and display novel electronic and magnetic properties.16 There have been many investigations in graphene nanoribbons (GNRs)17–19 but the structure imperfections at the edges have been the greatest challenge.20–22 It is anticipated that GNRs with edges passivated by hBN could overcome such a challenge.

Similarly, stacked graphene/hBN structures have also been intensively investigated.12–14 The lattice orientations of graphene and hBN can either be rotated (turbostratic stacking: Figure 1b) or aligned (in this case, there are three scenarios: AA stacking (Figure 1c), Boron-centered AB stacking (Figure 1d), and Nitrogen-centered AB stacking (Figure 1e)). Ab initio density functional calculations suggested that the most energetically favorable structure is the Nitrogen-centered AB-stacking, and in all three cases, the graphene will have an induced ~50 meV bandgap due to the asymmetry generated in the graphene lattice by the neighboring hBN layer.23 It was also

Received: October 9, 2012
Revised: February 12, 2013
Published: February 15, 2013

dx.doi.org/10.1021/nl303760m | Nano Lett. 2013, 13, 933–941
suggested that the bandgap of graphene increases as the interlayer distance decreases, with the largest bandgap of 0.55 eV at a 2.8 Å interlayer distance.24

Despite the enormous interest in hBN/graphene hybrid structures, there has been very limited experimental success in achieving these structures.7,25–28 L. Ci et al. demonstrated the synthesis of atomic layers of randomly distributed hBN and graphene domains, which enables the realization of a new material with distinct properties that are different from either graphene or hBN.25 Nevertheless, there is no control regarding the arrangement of B, C, and N atoms in these structures.28

More recently, Levendorf et al. and Sutter et al. have been demonstrated the synthesis of graphene and boron nitride lateral heterostructure on copper foil and Ru(0001), respectively.27,28 Both studies present the possibility of the synthesis of only lateral heterostructure.

In this work, we report for the synthesis of discrete graphene and hBN flakes patched as well as stacked together and investigated how the two materials merge with each other during synthesis. Two synthesis routes were explored, and in each case both in-plane and stacked junctions were observed by controlling the synthesis conditions. The studies carried out here can be applied to the synthesis of well-ordered hBN/graphene hybrid structures (such as graphene nanomesh or patterned GNR passivated by hBN).15,17,29,30 This highlights a promising direction for the synthesis and fabrication of future two-dimensional electronics.

**Results and Discussion.** The first route is by growing hBN flakes on copper foil first, using a low pressure chemical vapor deposition (LPCVD) system and ammonia borane as the precursor.31 Then, simultaneously, the ammonia borane source is turned off to terminate the hBN growth, methane is introduced and hydrogen gases are adjusted to the graphene synthesis condition (in this process the growth chamber and the Cu foil substrate remain at the same temperature, as graphene and hBN are both grown at 1000 °C). The samples grown by this way will be labeled hBN-G. The other synthesis route explored was by allowing graphene to grow on Cu foil under LPCVD at 1000 °C first, then immediately followed by hBN growth. The samples grown in this second route will be labeled G-hBN.

A general summary for the hBN-G growth is outlined here: The hBN flakes are unstable at the 1000 °C growth temperature in an H₂ environment on Cu, which could be due to the finite solubility (~0.29 at.% around 1013 °C) of Boron in Cu,32 or due to the H₂ etching effect (i.e., BN + H₂ → BH₃ + NH₃).33 Therefore in order to grow graphene at 1000 °C with hBN flakes on Cu, the graphene growth time has been limited to 10–20 s. In our synthesis, different CH₄ concentrations and different growth times were experimentally investigated (see Supporting Information Figure S1). When the methane concentration is relatively low, it was observed that most of the graphene flakes grow from the edge of the hBN flakes; however, with higher methane concentration and longer growth time, denser and larger graphene flakes can nucleate on Cu directly, away from the hBN flakes.

Figure 2a shows the SEM image of a typical hBN-G structure on a copper foil grown with low methane concentration (1 sccm) and a short growth time (10s) (L-hBN-G, L indicating a low methane supply). The lighter color triangular flakes are hBN (the white triangular particles on the hBN flakes are the multilayer hBN stacks), whereas the circular darker flakes are graphene. Surface potential measurements of graphene and hBN flakes were carried out by measuring the contact potential difference (CPD) using scanning Kelvin probe microscopy (SKPM) (see Supporting Information for details).34 We were able to image the junction region directly on Cu (Figure 2b shows a representative SKPM image of one of the samples). Most of the hBN-G junctions we find in the L-hBN-G samples suggest that the hBN and graphene regions form an in-plane junction, as illustrated in Figure 2c and Figure 2d. The SKPM image in Figure 2b shows that the measured effective surface potential (V_{sur}) of graphene is higher than that of hBN, which allows us to easily characterize each region of graphene and hBN by SKPM. The samples were also characterized by AFM after transferred to the 300 nm SiO₂/Si substrate (Figures 2e and 2f). In the height image, the graphene and hBN regions cannot be distinguished from each other, providing further evidence that the two regions have merged into one plane.

We further characterized these samples using atomic resolution annular dark-field (ADF) imaging in an aberration-
corrected scanning transmission electron microscope (STEM).35 The microscope was operated at 60 kV to avoid electron beam damage to the hBN and graphene materials. Figure 2g is a high-magnification medium angle (MA)ADF STEM image of a monolayer hBN region, and the fast Fourier transform (FFT) obtained indicates a hexagonal atomic structure. Individual boron and nitrogen atoms are clearly distinguished by their different intensities B (atomic number $Z = 5$) as shown in red and N (Z = 7) as shown in blue in Figure 2g.36 Figure 2h shows a line profile along the direction marked in Figure 2g. We estimate that the lattice distance between the boron atom and the nitrogen atom is 1.45 Å. This value agrees well with previous observation on bulk hBN material.36 Figure 2i shows a high-magnification MAADF image of a monolayer graphene region; the FFT in the inset indicates a hexagonal structure (scale bar: 0.2 nm).

For the stacked structures observed in these H-hBN-G samples, Figure 3e and Figure 3f are schematic diagrams illustrating the proposed scenario: since the methane supply is high, graphene nucleates directly on Cu regions away from hBN takes (Figure 3e). As the graphene flake grows, it extends to a nearby hBN and forms a stacked junction. This scenario suggests that there is an interdependence between the nucleation location of the graphene flake and the type of junction at the hBN/graphene interface. For instance, if the graphene flake nucleates at the hBN edge, an in-plane junction is obtained; whereas if the graphene first nucleates on Cu and then grows over the top of an hBN flake, a stacked-junction is formed (Figure 3f). Therefore, both in-plane and stacked
graphene/hBN junctions could be obtained by controlling the methane concentrations.

To understand the effect of the hBN substrate on graphene, Raman mapping was carried out on an H-hBN-G sample transferred onto a SiO2/Si substrate.38 Figures 3g and 3h show the AFM phase image and Raman mappings (intensity ratio of the D band to the G band (ID/IG) obtained for the same area of the sample. For the graphene flake in the middle of Figure 3g, part of it is directly on SiO2/Si (G/SiO2), while the other part of it is on top of hBN (G/hBN). Correspondingly, the ID/IG of the graphene flake shows a distinctive difference depending on the underlying substrate (Figure 3h). The D band intensity for G/hBN is noticeably lower (4 times) than the D band intensity for G/SiO2 (See Supporting Information, Table S1). Figure 3i shows the representative spectra from the two regions. This is a striking observation; typically the same graphene flake has a similar D band intensity across its area, but the observation here gives strong evidence that hBN is a much better substrate for graphene than SiO2. Furthermore, there is a redshift in the G band frequency as well, as can be seen in Figure 3i. The G band frequency of the G/hBN region is at 1590 cm$^{-1}$, whereas for the G/SiO2 region the G band frequency is at 1601 cm$^{-1}$. The higher measured frequency for G/SiO2 is a consequence of p-doping arising from the SiO2 substrate due to dangling bonds, charge traps as well as the organic residues left behind during the PMMA transfer process.39–41 Consistent results were observed on other graphene flakes (partially on hBN and partially on SiO2/Si) throughout the sample. The present work is the first systematic Raman characterization to compare the effect of two different substrates. The result suggests that the hBN flake underneath is protecting the graphene from being doped by the SiO2 substrate, preventing dangling bonds and charge traps accessing the graphene. It is observed that there is still a noticeable D band for the graphene on an hBN flake, possibly due to the residue impurities of boron on the copper surface which could affect the graphene quality during graphene growth. The lowered G’ intensity is also likely related to the higher frequency D band in this sample.

High magnification MAADF STEM was also used to further characterize the stacked hBN-G structures. Figure 4a is a MAADF STEM image of one flake with a Moiré pattern, and the corresponding FFT for this region (Figure 4b) shows five sets of hexagonal diffraction spots that arise from five rotated layers. Figure 4c zooms in at a particular set of the FFT spots. Since the lattice distance of hBN ($a = 2.504$ Å) is slightly larger than that of graphene ($a = 2.465$ Å), the three sets of the hexagonal FFT spots with a larger reciprocal lattice distance belongs to the graphene lattice, while the other two sets come from the hBN lattice. The rotational angles between these layers are indicated in Figure 4c. Thus the observed region in Figure 4a captures the stacking region of a three layers graphene that spreads on top of a bilayer hBN as illustrated by...
Figure 4d. In Supporting Information Figure S3 another region with a 2° rotational angle between a monolayer graphene and a monolayer hBN can also be seen. The STEM images reveal that the stacked layers in H-hBN-G sample typically show turbostratic stacking. Considering that the graphene flakes nucleate directly on the Cu substrate independently from the hBN flakes, it is anticipated that the graphene and hBN will very likely have different lattice orientations. Thus when a graphene flake extends on top of its nearby hBN, a turbostratic stacking should result. For the region shown in Figure 4a, electron energy-loss spectroscopy (EELS) was used to confirm the presence of B, C, and N (Figure 4e). A chemical quantification of the EEL spectra reveal a stoichiometry ratio of 51:49 (±5) between B:N, which is in pretty good agreement with the 50:50 theoretical ratio.

With the understanding gained through this first growth method (i.e., hBN-G growth), we next carried out the synthesis of G-hBN structures, that is, graphene flakes are first grown on Cu foil (1 min at 1000 °C), then immediately followed by hBN growth. The graphene growth condition was fixed and the hBN growth time was varied. This condition resulted in graphene flake edges serving always as nucleation sites for the hBN growth. With shorter growth time (7 min), mostly in-plane G-hBN structures were observed. With a longer growth time (10 min), the boundary between graphene and hBN served as nucleation sites for multilayer hBN flakes. Thus hBN/graphene stacked layers were obtained with longer growth time (hBN on top of graphene).

Figure 5a shows the SEM image of a typical G-hBN structure on copper foil following a 7 min growth of hBN. Compared with the graphene flakes without hBN growth (shown in Supporting Information Figure S4 as a reference), the graphene flakes in G-hBN appear smaller in size, suggesting that there is a slight etching effect for the graphene flakes during the hBN growth (similar to the hBN-G case). Since there is very low solubility of carbon inside Cu, this etching effect is most likely due to H2 etching. Nevertheless, this etching is much milder; therefore the hBN growth can last much longer. It can be seen in Figure 5a that all the graphene regions are enclosed by hBN flakes, implying that the hBN flakes grow from the edges of the graphene regions. The SKPM image shown in Figure 5b indicates that the hBN and graphene regions merged into one layer, thus forming an in-plane G-hBN structure. When using AFM to characterize the 7-min G-hBN sample transferred onto SiO2/Si, the graphene and hBN regions cannot be recognized in the height images (Figure 5c), providing further support on this. With longer growth time (10 min, Figures 5d-f), it can be seen that multilayer hBN flakes (the white triangular regions in the SEM image of Figure 5d) are grown at the boundary between the graphene and hBN monolayer regions. This can be also observed from the SKPM image in Figure 5e. For the 10-min hBN growth sample, multilayer flakes can also be recognized in the AFM height image (Figure 5f) at the boundary regions between the graphene and the hBN.

Resonant Raman spectroscopy was also used to characterize the G-hBN structure transferred on SiO2/Si. Figure 5g shows the Raman spectrum of a reference graphene film (bottom spectrum) (same sample from Supporting Information Figure S4) and two spectra from the graphene region in a typical G-hBN sample (middle spectrum is from region I, in the middle of a graphene flake, top spectrum is from region II, the edge region of the graphene flake). The top and middle spectra for the G-hBN has a small D-band and similar G’ band intensity as compared to the reference graphene. The
appearance of the small D-band suggests that the growth of hBN possibly induces some defects in the existing graphene lattice. However, the amount of defects appears to be much lower than for the hBN-G case. By comparing the top and middle spectra it can be seen that the graphene edge has a lower D band intensity, and this can be seen more clearly with the Raman ID/ISi mapping of a G-hBN flake in Figure 5h. It should be noted that ID/IG mapping shows very similar result with ID/ISi mapping. We chose ID/ISi mapping here, which is more distinct. The result is in sharp contrast to what is typically measured in graphene flakes with Raman spectroscopy, i.e., usually the edge region of a graphene flake shows a higher D band intensity than the inside region.44−46 This is the first observation that the D band intensity is lower for graphene edges when they are passivated by hBN. The finding serves as an exciting starting point for GNR research with hBN termination at a graphene edge.20−22

The 10-min grown sample was also further characterized by STEM, and one of the regions is shown in Figure 6a. Intensity profiles obtained in the region allow us to identify the number of layers of either hBN or graphene (see Supporting Information, Figure S5). The observed region captures the edge of a multilayer hBN that spreads on top of a monolayer graphene flake (as illustrated by Figure 6b). We observed up to 3 layers. In this area a GNR (in the upper left corner of Figure 6a) is also observed, forming a bilayer graphene region. The FFT image of the graphene/hBN hybrid region for the whole area is shown in Figure 6c. Here, one clear set of spots from the hBN stacks is seen. Upon closer examination, it is found that the diffraction spots arising from graphene do not exactly overlap with the hBN diffraction spots, and instead they have ~1° mis-alignment angle. A close up of the region with first hBN layer on graphene (1hBN/G) in Figure 6a reveals that the hBN hexagonal lattice overlaps with the graphene lattice, indicating that the first hBN layer has “AA-like”, slightly
twisted stacking with the underlying graphene layer. It is different from the AA-stacking as depicted in Figure 1(c), because from the FFT image it can be seen that here the hBN and graphene lattice constants are still different. This observation is in contrast to the theoretical predictions that AB-stacking is the most energy favorable structure between graphene and hBN. This is a strikingly intriguing observation; it calls for further theoretical investigations. It is also very interesting that the orientations between the top hBN and bottom graphene lattice do not exactly align with each other, and there is a ∼1° mis-alignment. Examinations at other areas of the sample (see SI, Figures. S6−S8 for three other locations) shows this <1° mis-alignment occurs in all those areas. At this stage, it is unclear what is the reason for the mis-alignment. Presumably as the multilayer hBN nucleates along the boundary between the graphene and the hBN, the lattice orientation of the underlying graphene dictates the lattice orientation of the multilayer hBN stack and there should be no mis-alignment. Possibly the lattice mis-match (∼1.7%) between graphene and hBN could be a reason for the observed <1° mis-alignment. Figures 6e−f show the EEL spectra for graphene (G) and two-hBN-layers-on-graphene (2hBN/G) regions in Figure 6a, further confirming the chemical composition of the two regions.

Figure 6. Lattice orientation alignment between the hBN and graphene layer in the 10 min G-hBN sample. (a) MAADF STEM images of the 10 min hBN growth sample (scale bar: 1 nm) (b) Schematic illustration of the multilayer hBN stacks grown at the graphene hBN interface (side view) as a possible scenario for (a). (c) The FFT pattern of the whole area in (a). (d) Zoom in at a particular region of the FFT spots (outlined with the orange square in (c)) reveals a lattice orientation mis-alignment of ∼1°. (e and f) EEL spectra of the G region (1 layer graphene) and 2hBN/G region (two-layers-hBN on 1 layer graphene) of the image in (a).

For the 2hBN/G region, examination of the lattice reveals that the second hBN lattice is displaced by half of unit cell with respect to the first hBN and graphene layers, thus indicating that the second hBN layer has AB stacking with the underlying hBN and graphene layers. There are totally 5 typical stable stackings for hBN layers: AA, AA’, AB (there are three cases for AB stacking, depending on the atoms that directly on top of each other in the two layers, they can be labeled as B−N AB, B−B AB, and N−N AB (see Supporting Information, Figure S9 for details and illustration). Theoretical calculation has suggested that among these five possibilities, AA’ and B−N AB are the most energy favorable ones. This means both AA’ and AB stacking should be observed experimentally. Although only AA’ was observed in X-ray diffraction originally, different TEM analyses have reported the observation of AB stacked hBN layers. The results suggest that our observation of AB stacking in the second hBN layer with the first hBN layer is not incidental. Although the discussion of the hBN stacking is not the main focus of this work, the finding here is really intriguing and requires further investigations.

Conclusion. In conclusion, an investigation was carried out in this work to obtain hybrid hBN and graphene structures by using the same Cu substrates but growing the two materials separately under CVD. Several interesting discoveries were encountered while examining the hybrid structures, the most intriguing one is the AA-like stacking between the hBN and graphene but with a mis-aligned angle consistently to be <1° in the G-hBN structures. In addition, these novel structures allow systematic Raman comparison of the same graphene flake on hBN and SiO2/Si substrates simultaneously, providing convincing evidence that substrate effect (doping, charge traps, or surface corrugation, etc) is also an important contribution to the D band intensity. When the graphene edge is passivated by hBN, Raman characterization shows that the D band intensity for the edge region is even lower than the inside graphene region. The characterizations used in this study reveal interesting phenomena related to the graphene-hBN growth and point to the necessity of gaining a better understanding of how the two materials merge with each other during the growth process. The growth methods demonstrated in this work open up opportunities for many proposed well-controlled graphene/hBN hybrid structures for future research and applications.
ACKNOWLEDGMENTS

The authors declare no competing financial interest.

REFERENCES


(40) Discussions among our own group with other groups at University of Southern California, N. U., and University of Illinois at Urbana−Champaign.


(50) Zan, R.; Bangert, U.; Ramasse, Q.; Novoselov, K. S. J. Microsc. 2011, 244 (2), 152−158.