

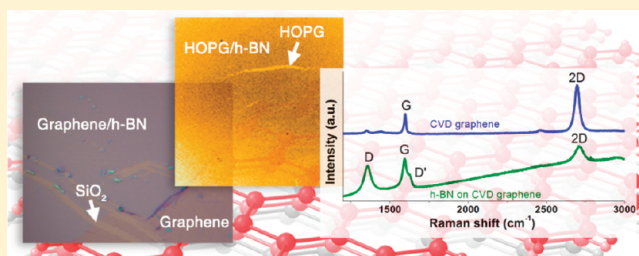
Direct Growth of Graphene/Hexagonal Boron Nitride Stacked Layers

Zheng Liu,[†] Li Song,[‡] Shizhen Zhao,^{†,§} Jiaqi Huang,^{†,||} Lulu Ma,[†] Jiangnan Zhang,[†] Jun Lou,^{*,†} and Pulickel M. Ajayan^{*,†}[†]Department of Mechanical Engineering & Materials Science, Rice University, Houston, Texas 77005, United States[‡]Research Center for Exotic Nanocarbons, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan[§]Department of Materials Science and Engineering and ^{||}Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

S Supporting Information

ABSTRACT: Graphene (G) and atomic layers of hexagonal boron nitride (h-BN) are complementary two-dimensional materials, structurally very similar but with vastly different electronic properties. Recent studies indicate that h-BN atomic layers would be excellent dielectric layers to complement graphene electronics. Graphene on h-BN has been realized via peeling of layers from bulk material to create G/h-BN stacks. Considering that both these layers can be independently grown via chemical vapor deposition (CVD) of their precursors on metal substrates, it is feasible that these can be sequentially grown on substrates to create the G/h-BN stacked layers useful for applications. Here we demonstrate the direct CVD growth of h-BN on highly oriented pyrolytic graphite and on mechanically exfoliated graphene, as well as the large area growth of G/h-BN stacks, consisting of few layers of graphene and h-BN, via a two-step CVD process. The G/h-BN film is uniform and continuous and could be transferred onto different substrates for further characterization and device fabrication.

KEYWORDS: Graphene, highly oriented pyrolytic graphite, hexagonal boron nitride, stacked films, chemical vapor deposition



As a typical two-dimensional material, graphene¹ has attracted wide attention. Graphene is a zero band gap semiconductor, with very high intrinsic room temperature carrier mobility.^{2,3} Recent works on graphene-based devices showed exciting potential in electronics and optoelectronics.^{4–8} However, the quality of the substrate supporting graphene seemed to have a high impact on the graphene properties, which was not desirable.^{2,4–6} Suspending graphene for devices would be technologically challenging. The other option will be to find a suitable substrate that supports graphene and retains its exciting electrical performance. Hexagonal boron nitride (h-BN),^{7–12} which is a two-dimensional material like graphene, perfectly flat and electrically insulating, seems to be such a unique candidate that it could serve as an excellent dielectric and substrate.^{7,9,12–15} h-BN has a large band gap and atomically smooth surface with minimum dangling bonds and charge traps. Furthermore, h-BN has a low dielectric constant, high temperature stability, and high thermal conductivity. In fact, recent experiments and theories have demonstrated that exfoliated h-BN film dramatically improved the current voltage characteristics of a graphene transistor.¹⁶ In contrast to exfoliation/peeling and heteroepitaxial techniques,¹⁷ a facile and scalable synthesis approach to making G/h-BN stacked structures will enable a lot of fascinating research in this area, including high-performance electronic,¹⁶ photonic devices,^{16,17} etc.

Traditionally, both graphene and h-BN films can be obtained by mechanical exfoliation from highly oriented pyrolytic

graphite (HOPG) and highly oriented pyrolytic boron nitride (HOPBN).^{18,19} Although this method can get crystalline flakes and layered samples, the thickness and size of samples are difficult to control. Recently, chemical vapor deposition (CVD) has been employed,^{14,20} providing an alternative approach to making graphene. Large-area and single-, bi-, and few-layer graphene have been grown on Cu substrates with methane gas as a precursor.²⁰ We recently also demonstrated that high-quality graphene could be obtained using *n*-hexane as a liquid carbon source.²¹ In addition, we were the first to report the successful CVD growth of two-dimensional atomic layers of h-BN films over large areas on copper and their transfer onto many substrates.¹³ In this Letter, we demonstrated the direct CVD growth of h-BN on HOPG and mechanically exfoliated graphene as well as a controllable large scale growth sequence for graphene/h-BN (G/h-BN) stacked structures, by combining the CVD growth processes that have been used for graphene and h-BN. The procedure is illustrated in Figure 1. High-quality and large-area graphene films were first grown based on optimized liquid precursor CVD method. In detail, the Cu foil (25 μ m thickness) was washed by diluted nitric acid (HNO₃:H₂O = 1:3) and deionized water for a few seconds to remove the surface oxidized layer and then loaded into the center of a quartz tube, as

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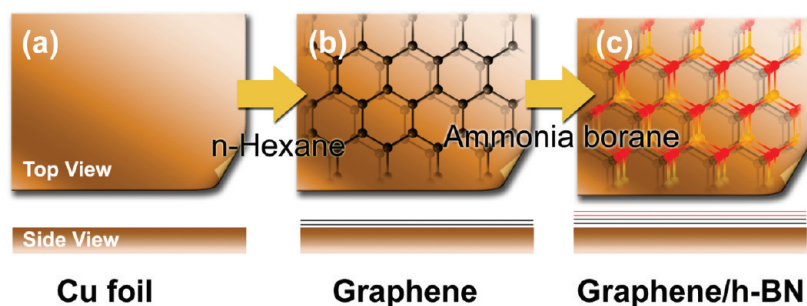


Figure 1. Schematic showing the preparation of G/BN stacked film. (a) The Cu foil is cleaned and prepared as the growth substrate. (b) High-quality and large-area graphene film is grown based on chemical vapor deposition process with *n*-hexane as a liquid carbon source at a temperature of 950 °C. (c) Some graphene is transferred onto SiO₂ substrates for further characterizations, and the rest is loaded into another furnace for the growth of h-BN film on top.

shown in Figure 1a. The growth temperature was raised to 950 °C with 500 mT Ar/H₂ gas flow (15 vol % H₂ balanced by 85 vol % argon) to avoid the oxidation of copper. Ar/H₂ gas was cut off when the temperature reached 950 °C, and then 150 mTorr *n*-hexane (C₆H₁₄) vapor was introduced into quartz for about 10 min. A fast annealing process was carried out at a rate of 50 °C/min under the protection of 500 mT Ar/H₂. The graphene films were grown continuously on Cu foil as shown in Figure 1b. The as-prepared graphene/Cu foils were then cut into two portions. One portion was transferred to SiO₂ substrates as reference samples for further characterizations. The rest was loaded into the center of another furnace to grow the h-BN film. Meanwhile, bulk HOPG (10 mm × 10 mm × 2 mm) and mechanically exfoliated graphene were loaded for direct growth of h-BN film on them, and a fresh copper foil was loaded together in order to obtain pure h-BN film as the reference sample. The samples were annealed at 800 °C for 20 min in 800 mT Ar/H₂ flow. The furnace was then heated up to 1000 °C for 20 min. Precursor ammonia borane (NH₃–BH₃) was sublimated at 130 °C by using a heating belt and then carried into the reaction region by Ar/H₂ gas flow. During the growth, Ar/H₂ gas was kept at about 400 mTorr. The typical growth time for h-BN was 10–30 min. After growth, the furnace was cooled down to room temperature quickly and the samples were transferred for further characterizations. Figure 1c illustrates the G/h-BN stacked film obtained on Cu foil after the above two-step CVD growth process. High-resolution transmission electron microscopy (HRTEM, JEOL-2100) and elemental mapping (Gatan GIF) were employed for imaging and chemical analysis of the samples. Field emission scanning electron microscopy (SEM, JEOL 6500F) was used to characterize the morphology of samples. Raman spectroscopy (Renishaw inVia) was performed with 514.5 nm laser excitation. X-ray photoelectron spectroscopy (XPS, PHI Quantera) was performed using monochromatic aluminum KR X-rays. Depth profiles were performed with accelerated voltage 3 kV Ar ion beam and alternative mode within an etching area of 2 × 2 mm to etch G/h-BN films. MultiPak software was used for XPS data analyses. Atomic force microscopy (AFM, Agilent PicoScan 5500 and Veeco Digital Instrument Nanoscope IIIA) was used to obtain film thicknesses and topographical variations in the samples.

The G/h-BN films were transferred onto Si/SiO₂ (285 nm) wafer for subsequent characterizations. The color of G/h-BN films looked like pristine h-BN film because the graphene layer underneath was too thin to be visible. The films were uniform and continuous after being transferred onto the substrates. Some

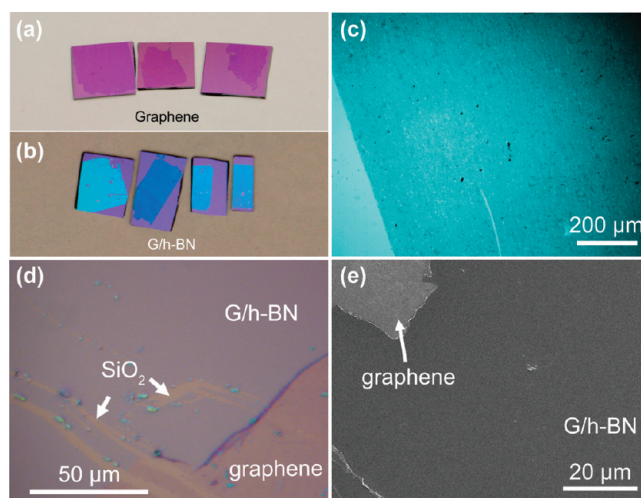


Figure 2. Optical and SEM images of graphene and G/h-BN stacks. (a, b) Photographs show the graphene and G/h-BN films on SiO₂ substrates. Graphene (purple), G/h-BN film (blue), and SiO₂ (light purple) could be identified by different colors. (c–e) Optical and SEM images of G/h-BN films. The films are uniform and continuous on the substrate. Some SiO₂ regions are visible after intended scratch to bare and show the graphene and G/h-BN regions clearly.

SiO₂ regions were exposed during scratching used to expose the landscape of the G/h-BN film. Panels a and b of Figure 2 are photographs of as-grown graphene and G/h-BN films on SiO₂ substrates, respectively. In fact, graphene, h-BN, and SiO₂ could be easily identified by different colors (graphene in purple, h-BN in blue, and SiO₂ in light purple). Panels c–e of Figure 2 show typical optical and SEM images of G/h-BN films, showing the films are uniform and continuous except for a few wrinkles, which may be caused during the transfer process or grain boundaries on the copper growth surface.^{20,22} HRTEM was performed to characterize the microstructure of G/h-BN films. Figure 3a shows the morphology of the thin film. HRTEM images indicate that the thicknesses of graphene and h-BN film are about two to a few layers, as typically shown in Figure 3b. With GIF (energy filtered images), we show the maps of the distribution of C, N, and B from selected areas as shown in Figure 3c. The elements are quite uniformly distributed in the imaged area according to panels d–f of Figure 3.

Raman spectroscopy with a 514.5 nm laser excitation was performed at a power of 20 mW. Raman spectra were recorded

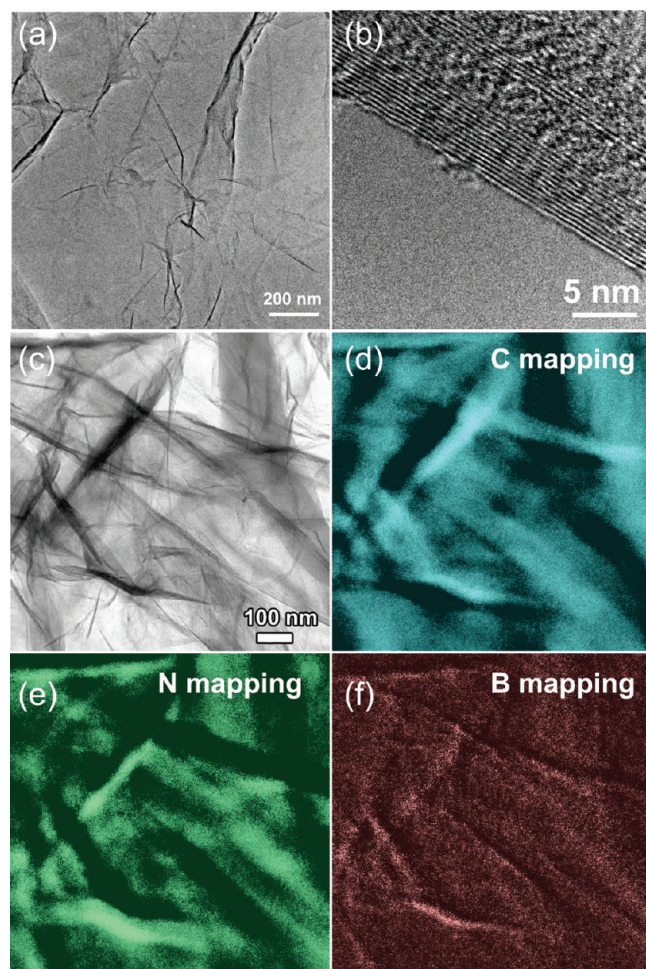


Figure 3. HRTEM images of G/h-BN film. (a) A TEM image shows the morphology of thin G/h-BN film. (b) An HRTEM image of the film edge shows the number of layers and thickness of the G/h-BN film. (c) Zero-loss TEM image. (d, e, and f) GIF imaging shows elemental distribution of boron, carbon, and nitrogen, respectively.

on the following samples: (1) h-BN powder and CVD-grown h-BN film (Figure 4a), (2) HOPG and HOPG/h-BN (see Supporting Information), (3) CVD-grown graphene and CVD-grown G/h-BN on SiO₂ wafer (Figure 4b), and (4) mechanically exfoliated graphene (ME-G) and ME-G/h-BN on SiO₂ wafer (Figure 4c). Figure 4a shows the Raman spectrum for a pure h-BN powder and CVD-prepared h-BN film. For the h-BN powder, the strongest peak is at $\sim 1369\text{ cm}^{-1}$ originating from the E_{2g} mode of B–N vibration. The peaks can be identified in the pristine h-BN film as the black arrows indicated.²³ For the CVD-prepared pure graphene, the disorder-induced Raman D-peak at $\sim 1350\text{ cm}^{-1}$ is weak, indicating the good quality of graphene grown by our vacuum-assisted CVD with liquid carbon source (Figure 4b). The G and 2D peaks can be found at 1597 and 2695 cm^{-1} , respectively. The intensity of the 2D peak is more than twice (~ 2.29) that of the G peak for most areas of the sample indicating the presence of one or two layers of graphene.^{20,24} This is further confirmed by the FWHM of 2D peak ($\sim 41.2\text{ cm}^{-1}$).^{25,26} After growing h-BN on it, several peaks are seen at 1356 cm^{-1} (may originate from the E_{2g} mode of B–N vibration $\sim 1370\text{ cm}^{-1}$ and D mode of graphene $\sim 1350\text{ cm}^{-1}$), 1595 cm^{-1} (from G mode of graphene),

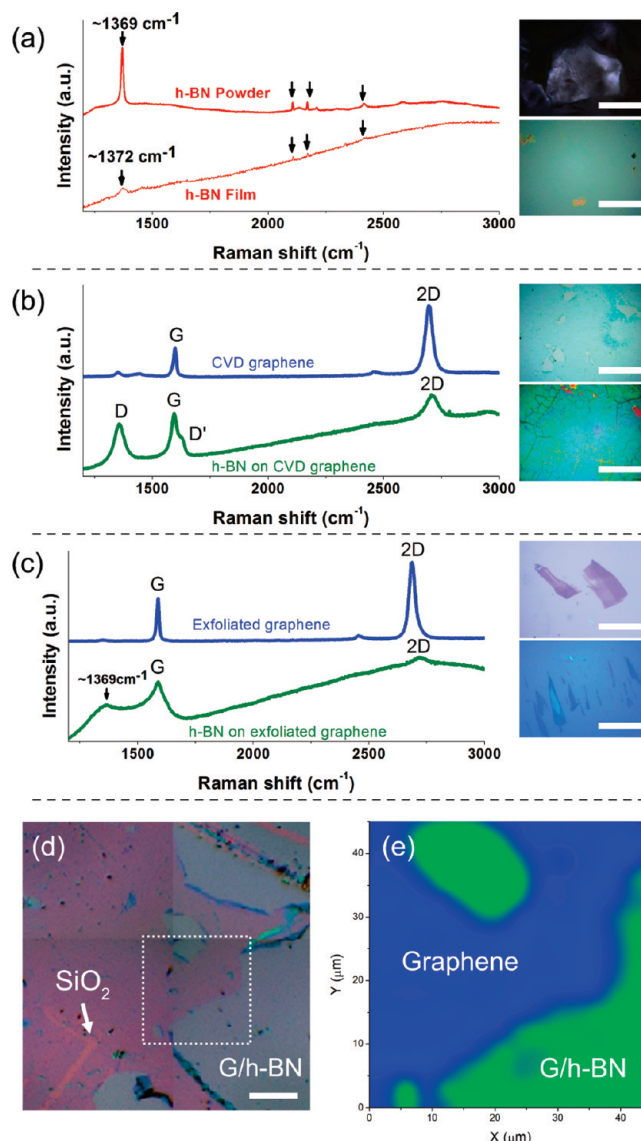


Figure 4. Raman spectra of h-BN and G/h-BN. (a) h-BN powder and pristine h-BN film show typical Raman peak at $\sim 1670\text{ cm}^{-1}$ and some additional weak peaks, indicated by arrows. (b) Pristine CVD graphene and h-BN on CVD graphene, implying one or two layers for graphene and corresponding peaks after growing h-BN on it. (c) Mechanically exfoliated graphene and after growth of h-BN on it. Insets in (a–c) correspond to optical images showing the areas from where Raman data were collected. (d) Optical image shows the morphology of G/h-BN film, and corresponding Raman mapping from the dotted area with the signal obtained at 2700 cm^{-1} in (e). Graphene and G/h-BN film areas are in blue and green, respectively.

1622 cm^{-1} (D' mode of graphene), and 2710 cm^{-1} (from 2D mode of graphene), respectively. These results are distinctively different from our previous report on hybridized boron nitride and graphene domains (h-BNC) and pristine h-BN.²⁷ In our previous work, it was found that the Raman peaks of h-BNC film were induced by hybridized graphene and h-BN domains together, which showed a mixed broad D band at 1360 cm^{-1} and a mixed suppressed 2D band at 2700 cm^{-1} . For the G/h-BN stacked structure, Raman peaks originate from the vibrational modes corresponding to h-BN and graphene independently. Therefore, one can clearly see the photoluminescence in whole

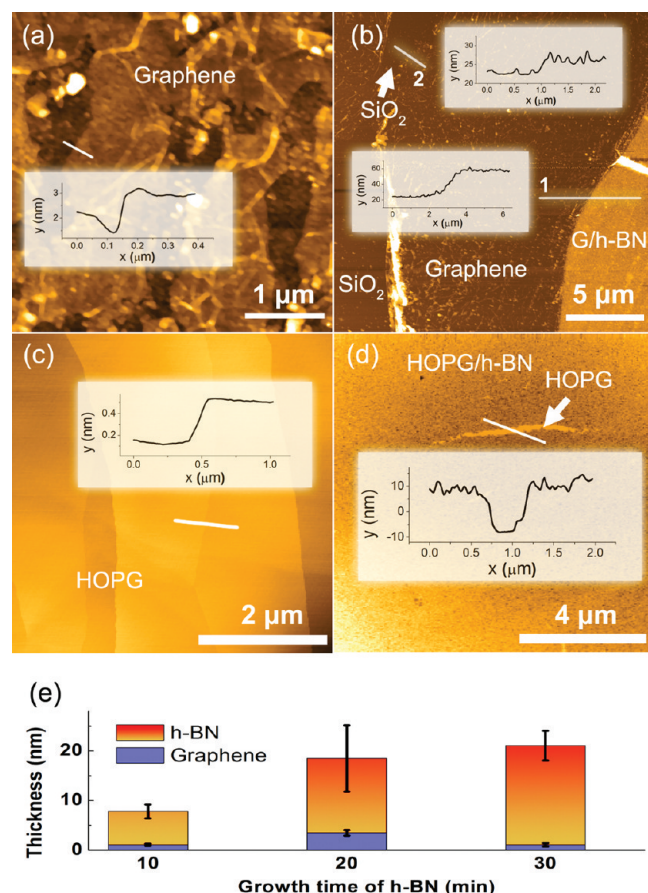


Figure 5. AFM images of G/h-BN and HOPG/h-BN films: (a) pristine CVD-prepared graphene, (b) h-BN on CVD-prepared graphene, (c) HOPG and (d) h-BN on HOPG. Insets are the cross sections in (a–d), respectively. (e) Three samples with increasing growth time of the h-BN film.

spectrum background induced by the top h-BN layers and the intrinsic characteristic G and 2D peaks contributed from the bottom graphene layers.

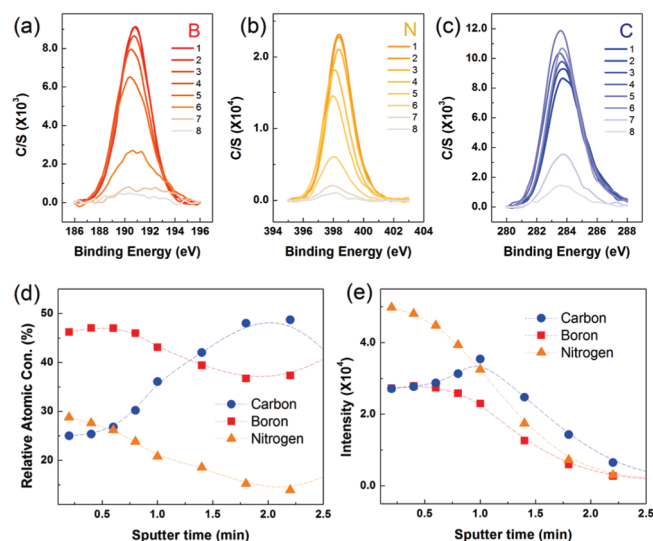
To further confirm that h-BN could indeed be grown on graphene, we collected Raman spectra on mechanically exfoliated HOPG (and directly on an HOPG block, see Supporting Information) before and after growing h-BN on them (see Figure 4c). The thickness of h-BN on HOPG ranges from 4.8 to 14.1 nm for different growing conditions. The Raman results were similar to Figure 4b with a stronger peak at $\sim 1369\text{ cm}^{-1}$. The photoluminescence background is also found in such samples. Furthermore, the thickness of graphene and h-BN make a great impact on their Raman signal. h-BN on HOPG block shows strong G and 2D peaks (see Supporting Information). The optical images shown in the insets of Figure 4a–c were the corresponding areas where Raman data were collected. Figure 4e is a Raman mapping taken from the dotted area ($45\text{ }\mu\text{m} \times 45\text{ }\mu\text{m}$) indicated in Figure 4d at a wavenumber of $\sim 2700\text{ cm}^{-1}$. There are a total of 256 (16×16) Raman spectra collected from this area. Graphene and G/h-BN areas are displayed in blue and green, respectively. The SiO_2 is marked with a white arrow. Raman spectra suggest good quality and uniform and continuous coverage of graphene and h-BN on the surface of the growth substrate (Cu).

AFM images show a clear stacked structure for G/h-BN samples. Panels a and b of Figure 5 are the topography of the

CVD-grown graphene and corresponding G/h-BN films. According to the cross-section analysis in Figure 5a, the thickness of graphene is around 1.1 nm. In fact, the thickness of graphene ranges from 1.0 to 3.5 nm for different samples, corresponding to two to several layers of graphene. Figure 5b shows a coexistence landscape of graphene, G/h-BN, and SiO_2 (substrate, marked by the white arrow). The step height is about 28.0 nm between graphene and G/h-BN (cross section 1) and 2.0 nm between graphene and SiO_2 (cross section 2). Panels c and d of Figure 5 show the heights of the HOPG surface steps and HOPG/h-BN films. For the HOPG, the cross section in Figure 5c shows a height $\sim 0.38\text{ nm}$. For the HOPG/h-BN, the step height between HOPG and HOPG/h-BN is $\sim 14.1\text{ nm}$. We have not found any obvious relationship between the thickness of graphene and the growth time, while the thickness of h-BN ranged from 3.2 to 20.0 nm and has a clear dependence on the growth time. Figure 5e shows three samples with different growth times of 10, 20, and 30 min, respectively. The thicknesses of graphene and h-BN are (1.1, 3.5, and 1.1 nm) and (6.7, 15.0, and 20.0 nm) respectively.

The XPS spectra of the as-grown G/h-BN films and HOPG/h-BN for the B, N, and C edges are presented in Figure 6 by using the depth profile test, which provides additional information on the stacked layer structure. High-energy Ar ion beam with accelerated voltage of 3 kV was used to sputter the samples from its top surface layer by layer within an area of $2 \times 2\text{ mm}$. The evolution of counts/second (counts/s) during etching is shown in (a–c) and (f–h), for boron, nitrogen, and carbon, respectively. Both samples show a B 1s core level at 189.8–190.8 eV, which is almost identical to the bulk boron nitride with hexagonal phase that was reported previously.^{28,29} The N 1s peak is located at 398.2–398.6 eV, also very close to the reported position of the N 1s spectrum (398.1 eV).^{28,29} The C 1s peak is located at 284.2–283.7 eV, corresponding to the value (284.5 eV) in graphene.³⁰ The counts per second of boron and nitrogen decrease gradually because the h-BN film is becoming thin due to the Ar ion milling. Interestingly, we observed the counts per second of carbon increases first and then decreases for as-grown graphene/h-BN films. Panels d and e of Figure 6 show the evolution of atomic concentration and intensity for elements B, N, and C. The atomic concentration and intensity decreased for both boron and nitrogen with Ar ion etching time increasing, which suggests h-BN as the top layer of the as-grown stacked films. For carbon, Ar ion etching made an increase in its concentration and intensity initially, followed by a decrease. We can explain this by considering that h-BN layer grew on the graphene layer. With the Ar ion etching, the top h-BN layer becomes thinner and the buried graphene layer appears resulting in the maximum value of carbon concentration in XPS data. Then the value decreases because graphene also gets removed by the continuous ion etchant. The stacked structure with h-BN on top and G below is further supported by the XPS depth profile for HOPG/h-BN. Ar ion etching decreases the boron and nitrogen's atomic concentration and intensity and eventually brings them to zero. Accordingly, the concentration and intensity of carbon increase, as the HOPG substrate is exposed by the removal of h-BN grown on top.

It was reported that monolayer h-BN can be grown on transition metal surfaces under vacuum conditions resulting from the thermal decomposition of borazine at a high temperature.^{8,31,32} A large scale growth of atomic h-BN layers has been further demonstrated on copper and nickel films using

CVD-Graphene/h-BN on SiO₂

h-BN on HOPG

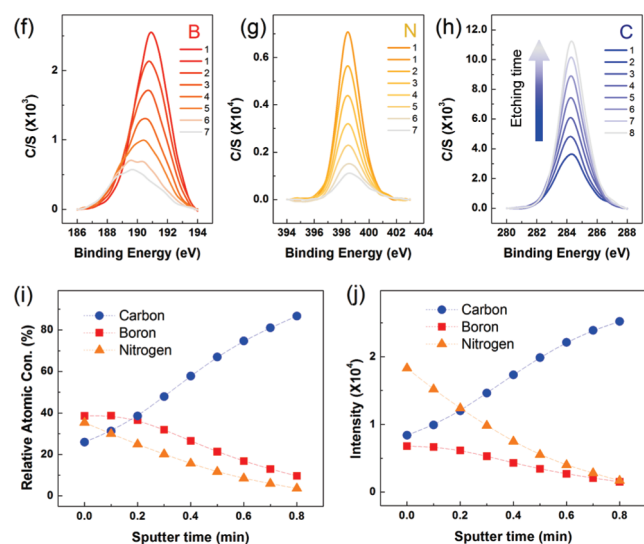


Figure 6. XPS depth profiles of G/h-BN and HOPG/h-BN films. (a–e) and (f, g) are results for h-BN on CVD-prepared graphene and h-BN on HOPG, respectively. (a–c) and (f–h) show the evolution of counts per seconds for B, N, and C 1s core levels during etching with Ar ion. The signals from B and N become weak during etching. The strongest signal from C is obtained after etching for about 1 min. (d, e) and (i, j) are their relative atomic concentration and intensity with increasing etchant time.

ammonia borane and borazine.^{13,14} The selective growth of h-BN on graphene may result from their similar conformation,³³ which is confirmed by a recent work of growing graphene on h-BN single crystal flakes.³⁴

In summary, we demonstrated the direct growth of h-BN on HOPG and mechanically exfoliated graphene, as well as via a two-step sequential CVD growth process for the scalable growth of few layer G/h-BN stacked films. Graphene was grown on Cu foil first using a liquid carbon source, and h-BN film was then grown with ammonia borane under optimized parameters. Raman spectra show graphene and h-BN film stacked together

uniformly with good quality. AFM images confirm that the h-BN films were grown on top of graphene layers, and depth profiling using XPS further proves this hypothesis. Our synthesis method could open up new avenues for exploiting the properties and applications of atomically thin G/h-BN heterostructures.^{17,35}

■ ASSOCIATED CONTENT

S Supporting Information. Additional description of Raman spectra of HOPG/h-BN and current-sensing atomic force microscopy (characterization of HOPG/h-BN. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jlou@rice.edu (Jun Lou); ajayan@rice.edu (Pulickel M. Ajayan).

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