Chemical Interaction-Guided, Metal-Free Growth of Large-Area Hexagonal Boron Nitride on Silicon-Based Substrates

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Supporting Information

ABSTRACT: Hexagonal boron nitride (h-BN) is an ideal platform for interfacing with two-dimensional (2D) nanomaterials to reduce carrier scattering for high-quality 2D electronics. However, scalable, transfer-free growth of hexagonal boron nitride (h-BN) remains a challenge. Currently, h-BN-based 2D heterostructures require exfoliation or chemical transfer of h-BN grown on metals resulting in small areas or significant interfacial impurities. Here, we demonstrate a surface-chemistry-influenced transfer-free growth of large-area, uniform, and smooth h-BN directly on silicon (Si)-based substrates, including Si, silicon nitride (Si₃N₄), and silicon dioxide (SiO₂), via low-pressure chemical vapor deposition. The growth rates increase with substrate electronegativity, Si < Si₃N₄ < SiO₂, consistent with the adsorption rates calculated for the precursor molecules via atomistic molecular dynamics simulations. Under graphene with high grain density, this h-BN film acts as a polymer-free, planar-dielectric interface increasing carrier mobility by 3.5-fold attributed to reduced surface roughness and charged impurities. This single-step, chemical interaction guided, metal-free growth mechanism of h-BN for graphene heterostructures establishes a potential pathway for the design of complex and integrated 2D-heterostructured circuitry.

KEYWORDS: hexagonal boron nitride, graphene, heterostructure, CVD, interface, FET

Hexagonal boron nitride (h-BN) has remarkable physical properties and chemical stability with a wide variety of applications, including ideal gate dielectrics for graphene and other two-dimensional (2D) nanomaterials electronics, a deep ultraviolet emission device, the world’s thinnest tunneling junction, a proton exchange membrane, and a high chemically tolerant film for protective coatings. Several techniques have been employed to synthesize thin films of h-BN, including micromechanical cleavage, chemical exfoliation via ultrasonication, atomic layer deposition, and chemical vapor deposition (CVD). Although CVD can be used to produce h-BN domains on catalytic metal surfaces, relocating h-BN from the metal surfaces onto other desired dielectric substrates requires an additional wet/dry transfer process, which introduces unintentional surface corrugations and possible adsorption of polymeric impurities on the h-BN surfaces. For 2D electronics and industry-level scalability, a direct, transfer-free, and large-area synthesis of h-BN films on dielectric substrates is critically needed. Although a few recent studies have demonstrated the growth of amorphous, nanocrystalline, or polycrystalline h-BN films on silicon (Si)-based surfaces via CVD, the growth mechanism is not fully understood.

Received: March 8, 2017
Accepted: April 25, 2017
Published: April 25, 2017

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Toward scalable manufacturing of interfacial polymer-free graphene/h-BN heterostructures, we introduce here two findings: (i) the h-BN growth, thickness and smoothness are influenced by the chemistry on the Si-based surfaces including Si, silicon nitride (Si₃N₄), and silicon dioxide (SiO₂). (ii) Demonstration of the polymer-free interfacing of graphene on metal-free, large-area, directly grown h-BN films. The smooth surface and low surface charge inhomogeneity of the CVD grown h-BN substrate play an important role in the 3.5-fold enhancement in CVD grown graphene’s charge carrier mobility.

RESULTS AND DISCUSSION

The h-BN syntheses on Si₃N₄/Si substrates were performed via a low-pressure CVD (LPCVD) system as described in the Materials and Methods Section. The quality and uniformity of h-BN films were analyzed by confocal Raman spectroscopy, which exhibits a singular peak centered at 1372 cm⁻¹ corresponding to the E₂g in-plane phonon mode (Figure 1a), affirming the formation of h-BN films. Further, a weak peak at about 1450 cm⁻¹ in Figure 1a demonstrates the third order transverse optical phonon mode for Si as the underlying substrate is Si₃N₄/Si (see Supporting Information section 1 for the Raman spectrum of bare Si₃N₄/Si substrate). The schematic of E₂g phonon mode for boron (B) and nitrogen (N) in-plane Raman vibrations is shown in the inset of Figure 1a. The focus of the current work is to produce metal-free, large-area, continuous, and uniform h-BN dielectric films on Si-based substrates without any transfer-associated processes. The directly grown h-BN’s microstructure was examined using transmission electron microscopy (TEM) for which the free-standing h-BN films were transferred onto TEM grids (see Materials and Methods Section for the transfer process). Figure 1e shows the atomic periodicity with lattice constant of 2.5 Å (see Supporting Information section 2) in the directly grown h-BN structure and the corresponding selected area electron diffraction (SAED) bright pattern (Figure 1f) confirms the h-BN’s hexagonal lattice. The bright spots in the SAED pattern correspond to the lattice spacing (d) of 1.54 Å, which implies lattice constant of 2.5 Å for the h-BN’s hexagonal lattice. Further, the bright spots in the SAED pattern represent (103) crystal planes of directly grown CVD h-BN and very interestingly, the (103) crystal planes of h-BN consists of either only boron (B) or nitrogen (N) atoms. It is also important to observe that the TEM micrograph and SAED pattern for a ∼200 nm diameter region predict that the h-BN formed is part polycrystalline and part nanocrystalline. In order to further confirm the formations of h-BN film on Si₃N₄/Si substrates, elemental composition and stoichiometry were analyzed via X-ray photoelectron spectroscopy (XPS). Figure 1b illustrates the optical image of h-BN thin film of 5 × 1 cm² area coverage on Si₃N₄/Si substrates. The continuity and uniformity of the directly grown h-BN films are clearly noticed by the homogeneous color contrast of the elastic light scattering (Rayleigh)-based optical microscopic image (Figure 1c) and inelastic light scattering-based Raman spatial mapping (Figure 1d), where the regions marked by red, blue, and black circles correspond to the consistent Raman spectra in Figure 1a.
1g and h present high resolution XPS spectra of B 1s and N 1s, respectively, fitted by the Gaussian function. The B 1s spectrum appears at binding energy (BE) of 190.30 eV and the N 1s signal appears at BE of 397.87 eV, and both the spectra are attributed to B−N bonding. The atomic concentration ratio of N and B is 1:1.11±0.09, illustrating the formation of almost equal composition of B and N elements in the synthesized stoichiometric h-BN films. Furthermore, because the surface of h-BN is atomically smooth, it is therefore important to quantify the degree to which this valuable characteristics of the h-BN layer isolates the surface roughness of the Si-based substrates. Figure 1i depicts the atomic force microscopy (AFM) measured roughness histograms fitted by the Gaussian distribution with standard deviations of 0.66 nm for the h-BN deposited Si3N4/Si surfaces and 2.22 nm for the bare Si3N4/Si surfaces, implying a 3.4-fold increased surface smoothness for h-BN coated Si3N4/Si surfaces. This is further verified via AFM 3D topography images for Si3N4/Si and h-BN/Si3N4/Si surfaces (see Supporting Information section 3).

The kinetics and mechanisms of h-BN growth on several metal surfaces have been identified (e.g., surface-mediated for Cu and segregation-based for Ni and Fe). However, an understanding of the influence of the surface chemistry on h-BN growth kinetics is critical for Si-based dielectric surfaces including Si, Si3N4/Si, and SiO2/Si. We found that the growth rate was faster for SiO2/Si (~6 nm in 60 min), followed by Si3N4/Si (~5 nm in 60 min), and Si substrate (~1 h-BN monolayer in >120 min). The schematic for the metal-catalyst-free h-BN growth process on Si-based surfaces is presented in Figure 2a. This CVD growth of h-BN is accomplished via the following four elementary steps: (1) The solid ammonia borane (AB, NH3BH3) undergoes sublimation at about 100 °C and is carried into the reaction zone by hydrogen (H2) gas flow of 30 sccm. Upstream to the reaction zone (below the growth temperature), the AB complex is thermally decomposed to H2, aminoborane (NH2BH2), and borazine (B3H6N3). (2) Boundary layer diffusion of NH2BH2 (g) and B3H6N3 (g) to reach the chemical sites of the surface. (3) These precursor molecules are adsorbed on the surface and dehydrogenated at 700−1100 °C. Further, the mixture of these active species interface with the chemical sites on the Si-based substrates and hence, the nucleation of h-BN domains starts. (4) As the reaction continues, the h-BN film produced acts as a diffusion barrier for the active species to reach the chemical sites on the Si-based substrates. The above four steps can be summarized as follows:

(1) Gas phase dissociations:

\[ \text{NH}_3\text{BH}_3(g) \rightarrow \text{NH}_2\text{BH}_2(g) + \text{B}_2\text{H}_6\text{N}_3(g) + \text{H}_2(g) \]

(2) Boundary layer diffusion of \( \text{NH}_2\text{BH}_2(g) \) and \( \text{B}_2\text{H}_6\text{N}_3(g) \) to reach the chemical sites of the surface.

(3) Surface adsorption and reaction:
\[
\begin{align*}
\text{NH}_2\text{BH}_2(g) + \text{B}_3\text{H}_6\text{N}_3(g) + 4S & \quad \Rightarrow \quad 4(\text{BN})-S + 5\text{H}_2 \\
\end{align*}
\]

where \(S\) is the active site of Si-based surfaces, and \(k_1\) is the rate constant of adsorption. The rate at which (BN)-S reacts at the surface of Si-based substrates is given by

\[
(\text{BN})-S \xrightarrow{k_1} h-\text{BN} + S
\]

where \(k_1\) is the rate constant of reaction.

(4) Active species diffusion and surface nucleation: The \(\text{NH}_2\text{BH}_2\) (g) and \(\text{B}_3\text{H}_6\text{N}_3\) (g) continue to diffuse through the h-BN formed in step 3 to reach the chemical sites of the surface for further nucleation of h-BN film (as per step 3):

\[
F = -D_{\text{eff}} \frac{dC}{dx}
\]

where \(D_{\text{eff}}\) is the effective diffusion coefficient and \(\frac{dC}{dx}\) is the concentration gradient of the active species (borazine-like molecules).

Further, it will be shown later that the activity and the number of adsorption sites on the substrate determines the overall rate of growth of h-BN. The above phenomena can be explained by a model for the growth of h-BN on Si-based substrates after precursor-diffusion through the h-BN already grown. This model results the following equation (see Supporting Information section 4 for detailed derivations), which is consistent with the Deal–Grove model for diffusion of oxygen (O) through SiO2 and thermal oxidation of Si:39

\[
l^2 h-\text{BN} + A l h-\text{BN} = B t
\]

where, \(l\) is the thickness of h-BN film, \(t\) is the growth time, and \(A\) and \(B\) are constants (see Supporting Information section 4).

The h-BN film thicknesses on SiN4/Si and SiO2/Si at different growth time fit well (solid line in Figure 2b) with the above eq 1. The fitting parameters are h-BN on SiN4/Si (\(A = 13.36, B = 1.5\)) and h-BN on SiO2/Si (\(A = 6.45, B = 1.1\)). After the first h-BN layer is covered on Si-based substrates, the precursors have to diffuse through the formed layer (assumed nanocrystalline h-BN domains) to reach the chemical sites on substrates. From eq 1, the rate of growth is \(dl/dt = B/(2l^2 A)\), where \(l\) is the thickness of the h-BN film. There exists two regimes in the growth model.

Accordingly, at the early stages of growth (\(l \sim 0\)), the rate is linear: \(dl/dt_{\text{early}} = B/A \propto k_1\) (rate constant of reaction) and for a faster reaction rate or higher \(k_1\) (for SiO2/Si compared to SiN4/Si), this linear regime is more distinguishable (as can be seen in Supporting Information section 5). Further, as per the fitting parameters, the h-BN growth rate on SiN4/Si (\(B/A = 0.11\)) is slightly less than that on SiO2/Si (\(B/A = 0.17\)), which is consistent with the proposed model and molecular dynamics simulations shown later. In contrast, at sufficiently long time or at the large h-BN thickness, the growth rate is expected to be same: \(dl/dt_{\text{large}} = B/l^2 D\) (diffusion coefficient). Further, as per the fitting parameters, the value of \(B\) for h-BN growth on SiN4/Si (\(B = 1.5\)) is nearly same as that for h-BN on SiO2/Si (\(B = 1.1\)), which is consistent with the proposed Deal–Grove model. Further, it is important to note that, we have also considered other potential growth mechanisms, such as surface mediation, segregation, layer by layer deposition, and epitaxial growth. However, since the h-BN growth rate is nonlinear (growth rate reduces with time implying diffusion through layers during growth), nonself-limiting (implying nonequilibrium process; h-BN grows continuously), and different among SiN4/Si, SiO2/Si, and Si substrates (implying importance of surface chemistry or of the interface between active molecules and surface sites), the proposed mechanism fits the data well.

The model derived above for the growth of h-BN films on Si-based substrates (SiN4/Si, SiO2/Si, and Si) clearly shows the importance of the interaction of active molecules with the surface sites. To further understand the effects of the substrates on the interfacing of the reactants, we performed atomistic molecular dynamics (MD) simulations using the LAMMPS package.30 The interaction between the atoms were modeled using the 6–12 Lennard-Jones potential and Coulombic interaction. The details of the simulation cell and the interaction parameters used are provided in the Materials and Methods section and in the Supporting Information section 6.

Here, two different densities of 0.02 and 0.06 B3H6N3/Å2 of borazine molecules were used to simulate the adsorption of these molecules on the SiO2/Si and SiN4/Si surfaces. For both the densities, the adsorption rate was slightly higher on the SiO2/Si than on the SiN4/Si surfaces.

We first discuss the adsorption of borazine molecules of lower density (0.02 B3H6N3/Å2). Initially these molecules will be attracted toward the substrate by the long-range electrostatic forces and once they are at the substrate, the short-range van der Waals and long-range Coulombic forces will keep them adsorbed on the substrate. Because of the polar nature of the borazine molecules, we observed that initially in the gas phase they tend to form planar 2D clusters. A few molecules that do not join these clusters quickly get adsorbed over the substrates as individual molecules. We observed that after 12 ps, there were four such borazine molecules adsorbed over SiO2/Si, whereas only one molecule was adsorbed over the SiN4/Si surface (Figure 2c). It was also observed that the time required for the adsorption of all the molecules from the gas phase to the substrate (including those in clusters) was approximately 75 and 200 ps for SiO2/Si and SiN4/Si substrates, respectively. For the higher density of borazine molecules (0.06 B3H6N3/Å2), the adsorption rate was similarly higher for the SiO2/Si than for the SiN4/Si. For both surfaces, the borazine molecules form clusters and the total energy of the system equilibrates at approximately 20 ps. However, because of the higher density, all the borazine molecules formed planar 2D clusters, and the adsorption of single molecules recorded in the low-density case was not observed. Once again, the clusters were eventually adsorbed on the surfaces because of the long-range attractions. The time required for the borazine clusters to adsorb onto the SiN4/Si surfaces is three times higher than that required for the SiO2/Si surfaces (see Supporting Information section 6 and Figure S6).

The slightly higher adsorption rate of borazine molecules on SiO2/Si compared to SiN4/Si surfaces can be explained by the surface charge of the top layer of the substrates even though both the substrates maintain overall charge neutrality. The top layer of SiO2/Si (001) exclusively consists of dangling O atoms and the Si atoms are 1.24 Å below the surface O atoms (Figure 2c). So the top layer of the SiO2/Si substrate is negatively charged. Whereas, the top layer of the SiN4/Si (001) substrate has both Si and N atoms and the overall charge of the top layer...
is zero (Figure 2c). The negatively charged dangling O atoms in SiO2/Si tend to adsorb borazine molecules faster compared to the planar and neutral surface of Si3N4/Si. The adsorbed clusters will cover the surface and eventually undergo dehydrogenation and form h-BN films. Further, the h-BN layer will shield the electrostatic attractions and the rate will be determined by the rates of diffusion of the active species onto the substrate surfaces.

The experimental verifiﬁcation with the plausible growth model and subsequent MD simulations suggest that surface interfacing/reaction is the rate limiting step for h-BN nucleation on Si-based dielectric surfaces. In order to further conﬁrm the surface chemistry-guided mechanism, an experimental scheme was designed to grow h-BN on Si surfaces with and without O2-plasma treatment (see Supporting Information section 7 for the O2-plasma treatment procedures and surface characterizations). Further, it is challenging to grow h-BN on bare Si, however, by tweaking the kinetic factors during the growth (see Supporting Information section 8 for the CVD setup and growth conditions of h-BN on bare Si and O2-plasma treated Si surfaces), we formed large-area and continuous h-BN thin ﬁlms on Si substrates. As expected, the h-BN growth rate is higher on the O2-plasma treated Si surfaces in contrast to the bare Si surfaces as evidenced by the increase in Raman intensity of the h-BN’s E2g peak (Figure 2d), since high Raman intensity implies thicker ﬁlms. This conﬁrms that the h-BN growth rate is inﬂuenced by the chemical-interactions between the precursor complexes and the substrate surface. With minimal change in roughness before and after plasma treatment (see Supporting Information Figure S7), this result also shows that the substrate-roughness does not signiﬁcantly inﬂuence the growth. Further, the effects of growth temperature on h-BN formations on SiO2/Si and Si3N4/Si surfaces were examined via Raman spectroscopy as presented in Figure 2e. While the metal catalyst surfaces nucleate h-BN ﬁlms at a temperature of 750 °C, however, the h-BN formations on SiO2/Si and Si3N4/Si surfaces occurred at about 900 °C with no h-BN nucleation at 800 °C (Figure 2e), which may be attributed to the difference in the surface catalytic activity. Further, this is consistent with an earlier report on direct nanocrystalline h-BN formations on SiO2/Si substrates.18 Since high Raman intensity implies thicker h-BN ﬁlms, and because the Si3N4/Si surface allows weak interfacial attachment of precursor molecules, it nucleates thinner h-BN ﬁlms in comparison to SiO2/Si surfaces at different growth temperatures.

To verify the potential of directly grown h-BN for nanoelectronics, a monolayer and polycrystalline graphene ﬁlm with heavy grain density were grown via CVD and transferred onto h-BN/Si3N4/Si and Si3N4/Si substrates (see Materials and Methods Section for details of CVD growth of graphene and the transfer process). Such grain boundaries (coalesced grains: more detrimental or line defects: less detrimental) in graphene are known to reduce the carrier mobility32,33 and thus provide an estimate of how well the directly grown h-BN works to enhance the carrier mobility of heavy grain density graphene. Further, the grain-boundary
defects can be seen with the observation of D-bands in the Raman spectra of both the devices as shown in the Supporting Information section 9. The transferred polycrystalline graphene has noticeable D-band, which indicates high amount of grain boundaries, potentially coalesced grains (Figure S8). Figure 3a shows the schematic of a typical graphene/h-BN heterostructure without any polymer in the interface, a key design toward clean interfacial heterostructures, which is developed here. In order to comprehend the charged impurity effect of h-BN and Si₃N₄/Si substrates on the transferred polycrystalline graphene film, we have analyzed the doping density dependent parameters of the G-band position, full-width at half-maximum of G-band (fwhm(G)), 2D-band position, the ratio of intensities of the D- and G-bands (I_D/I_G), and the ratio of intensities of the 2D- and G-bands (I_2D/I_G) via confocal scanning Raman spectroscopy and spatial mapping. In Figure 3b, the G-band position of graphene on h-BN (denoted as “G/h-BN”) and graphene on Si₃N₄/Si (denoted as “G/SiN”) are predominantly centered at 1579.5 and 1582.7 cm⁻¹, respectively. The calculated fwhm of the graphene’s G-band is decreased from 29.0 cm⁻¹ (h-BN substrate) to 25.5 cm⁻¹ (Si₃N₄/Si substrate). Further, in Figure 3c, the 2D-band position for G/h-BN and G/SiN is centered at 2671.7 and 2680.5 cm⁻¹, respectively. In addition, the I_2D/I_G is found to be increased from 1.3 for G/SiN to 2.9 for G/h-BN. Here, it is critical to note that the CVD graphene synthesized on the same copper (Cu) foil of area 1 × 1 cm² were transferred onto Si₃N₄/Si and h-BN/Si₃N₄/Si surfaces. Hence, it is logical to imply that the density of graphene grains exist equally in both the samples, or in other words, they have similar I_D/I_G ratio. The observation of the softening of the G- and 2D-bands, the broadening of the fwhm(G), and the increase of I_D/I_G in addition to the high I_2D/I_G clearly signify a low charged impurity of graphene on h-BN substrates compared to the graphene on Si₃N₄/Si counterpart. The complete Raman spectra of G/h-BN and G/SiN along with the I_D/I_G are shown in the Supporting Information section 9 and Figure S8. Further, the increase of I_D/I_G in the case of G/h-BN can be attributed to the defects on graphene and the reduction of total scattering rate of photoexcited charge carriers on atomically flat h-BN substrate. In our device configurations, such charged impurities may originate from (i) photoresist residue (while fabricating field effect transistor (FET) devices as discussed later) and (ii) electron–hole puddling (bottom h-BN substrate). Since the processes of graphene FET device fabrications on h-BN and Si₃N₄/Si substrates are similar (see Materials and Methods Section) and the same graphene film was used in both cases, clearly the charge-donating impurities (n*) from the underlying substrates play a crucial role in our observations.

The charge inhomogeneity not only affects the Raman scattering parameters, but is also the dominant cause of scattering for carriers in G/h-BN/SiN (thickness of h-BN ∼ 5 nm) and G/SiN heterostructure FET devices. A schematic of a G/h-BN back-gate FET is shown in Figure 4a, with an optical image of the device (L/W of 27 μm/7.5 μm), which uses Cr/Au film (15 nm/95 nm) for contact electrodes (inset). Because both devices were fabricated using the same contact electrode materials with similar device treatments, a similar effect of contact resistances is expected on the electrical performances. Since it is characterized by lower charge fluctuations, the directly grown metal-free h-BN substrate platform developed here promises to enhance the charge carrier mobility in

Figure 4. Electrical transport properties. (a) Schematic of G/h-BN heterostructure device with inset showing the optical microscope image of the back-gated field effect transistor (scale bar is 20 μm). (b) Conductance vs carrier concentration characteristics of G/h-BN and G/SiN heterostructures at 15 K and V_D = 5 mV. (c) The carrier mobility values for both the devices at 15 K. (d) Variation of field effect mobility with carrier concentration for G/h-BN and G/SiN heterostructures at 15 K.
polycrystalline CVD graphene devices compared to high k dielectric substrate, i.e., Si$_3$N$_4$/Si in the present study.

Figure 4b shows that the conductance is strongly sublinear with respect to the carrier density. This indicates a crossover from low carrier densities, where scattering is dominated by the charged impurities, to large carrier densities where short-range impurity scattering is dominant. The data obtained (Figure 4b) can be fitted with a self-consistent Boltzmann equation for diffusive transport, which includes both long- and short-range scattering:

$$(\sigma)^{-1} = (n\mu_C + \sigma_{imp})^{-1} + \rho_S$$

where $\mu_C$ is density-independent mobility due to the charged impurity Coulomb (long-range) scattering, $\rho_S$ is the contribution to resistivity from the short-range scattering, and $\sigma_{imp}$ is the residual conductivity at the charge neutrality point (CNP). The detailed derivation of the self-consistent Boltzmann equation is outlined in the Supporting Information section 10. As shown in Figure 4c, the calculated mobility, $\mu_C$, is ~1200 cm$^2$V$^{-1}$s$^{-1}$ for high grain density graphene on h-BN (G/h-BN) FET device. This is ~3.5-fold higher than G/SiN, as a consequence of the Columbic scattering in G/h-BN device is lower than that of G/SiN device. Since it is known that a thicker h-BN film would result better isolation of charged impurities, we envision that carrier mobility and the minimum conductivity of G/h-BN device will be further improved with thicker h-BN films (h-BN thickness in our device is ~5 nm).

Further, the discussion on charge inhomogeneity point and the electron–phonon scattering is described in the Supporting Information section 11 along with the temperature dependence of sheet resistivity in the Supporting Information section 12.

It is well-known from the literature that the field effect mobility is defined as the derivative of the Drude formula, $\mu_{EF} = \frac{1}{\epsilon} \left( \frac{d\sigma}{dV_{bias}} \right)$. In the case of the G/h-BN (G/SiN) device, the $\mu_{EF}$ value varies from 500 cm$^2$V$^{-1}$s$^{-1}$ (250 cm$^2$V$^{-1}$s$^{-1}$) at high densities to ~1200 cm$^2$V$^{-1}$s$^{-1}$ (350 cm$^2$V$^{-1}$s$^{-1}$) near the CNP (see Supporting Information section 13 for the charge carrier mobility results for both back-gate FET devices at 300 K). This further confirms the enhancement of polycrystalline graphene’s mobility on directly grown h-BN substrates in comparison to Si$_3$N$_4$/Si substrates over the entire carrier density regime as shown in Figure 4d.

CONCLUSIONS

In summary, large-area, van der Waals interaction-bound, polymer interface-free, and electronically isolated graphene/h-BN heterostructures were produced. We describe the surface chemical interaction influenced mechanism for transfer-free h-BN formations on Si-based oxide (SiO$_2$/Si) and nitrile (Si$_3$N$_4$/Si) surfaces, supported by MD simulations. Interestingly, the low-temperature electronic transport measurements reveal that the CVD graphene with heavy grain on directly grown h-BN heterostructure devices exhibit improved charge carrier mobility (3.5-fold enhancement) compared to graphene on Si$_3$N$_4$/Si FET devices. The scalable and versatile method of direct production of h-BN-based heterostructures developed here is compatible with the semiconductor industry’s current production methods. This process can enable manufacturability of a variety of intelligently designed 2D heterostructures with applications ranging from nanoscale electronics to energy conversion and optoelectronics.

MATERIALS AND METHODS

Synthesis of Hexagonal Boron Nitride (h-BN) on Si-based Substrates and Characterizations. The h-BN synthesis was performed via a low-pressure chemical vapor deposition (LPCVD) system (MTI OTF-1200X) with a specially designed separate chamber for ammonia-borane (AB) solid precursor. The silicon (Si)-based substrates (Si$_3$N$_4$/Si and SiO$_2$/Si) supplied by SunEdison Semiconductor were cleaned using piranha solution (a volumetric mixture of 3:1 of 98% H$_2$SO$_4$ and 35% H$_2$O$_2$). For h-BN synthesis, the substrates were directly placed in the center of quartz tube’s heating zone and heated to 1100 °C in H$_2$ atmosphere to restrict further oxidation. As soon as the tube heating zone reached a temperature close to 1100 °C, the AB was sublimed at ~100 °C, and transported to the chamber (by opening the valve) containing the substrates via supplied H$_2$ carrier gas at a flow rate of 30 sccm. The h-BN synthesis takes place at a temperature of 1100 °C, a pressure of 5–10 Torr, and the reaction time was varied from 15 to 120 min followed by fast cooling (~100 °C/min) of the CVD chamber. Meanwhile, the chamber containing AB was also cooled down to room temperature and the valve was closed in order to stop supply of AB into the main CVD chamber which contains the substrates. The synthesized thin films of h-BN were characterized by a combined confocal Raman-atomic force microscopy (Raman-AMF, WITec alpha300 RA, laser wavelength of 532 nm), transmission electron microscopy (TEM, JEOL JEM-3010, operated at 300 kV), and X-ray photoelectron spectroscopy (XPS, Kratos AXIS-165). For the AFM measurements of h-BN surface roughness and film thickness, the h-BN thin film surfaces were patterned through microfabrication etching processes: UV photolithography (Karl Suss MA6) and reactive ion etching (Oxford Instruments).

Transfer of h-BN Films onto TEM Grids. The TEM sample preparation was performed as follows: First, 25 mg/mL of poly(methyl methacrylate) (PMMA) (MW 996,000; Sigma-Aldrich) in anisole (99% purity; Acros Organics) was spin-coated onto the h-BN/Si$_3$N$_4$/Si substrate at (i) prespin of 500 rpm for 5 s and (ii) full-spin of 4000 rpm for 30 s. The PMMA-coated h-BN/Si$_3$N$_4$/Si substrate was then air-dried for 5 min, followed by etching of the Si$_3$N$_4$/Si substrate with 30% of KOH for 8 h. The floating PMMA/h-BN sample was picked up by submerging a clean metal spoon into the solution, and lifting up at 40° angle to the surface of etchant solution. Immediately, it was transferred onto DI water at the same manner as previous picking up step (repeated three times). The floating PMMA/h-BN in DI water was picked up by a carbon film TEM grid with 40° angle to the surface of the DI water. After the PMMA/h-BN/TEM grid is air-dried overnight, the acetone solvent was drop-casted via glass pipet to remove PMMA, and then air-dried for 5 min (repeated 2–4 times). Subsequently, IPA solvent, and water were drop-casted via glass pipet and air-dried for 5 min (repeated 2–3 times). Then the free-standing h-BN on TEM grid samples were analyzed by TEM.

Molecular Dynamics Simulations. To model the adsorption of the borazine molecules on the surface, we used all-atom interaction potentials. The van der Waals interaction is modeled using the 6–12 Lennard-Jones potential and the electrostatic potential is modeled using the Coulomb’s law. The details of the simulation cell and the interaction parameters used are provided in Supporting Information section 6. The adsorption of borazine molecules on SiO$_2$/Si and Si$_3$N$_4$/Si substrates were studied using NVT ensemble simulations at a temperature of 1000 K. In the entire simulation, only the borazine molecules were kept mobile and further, the molecules were treated as rigid bodies and the force on each molecule is the sum of forces on all 12 atoms in the molecule ($B_3H_6N_3$). The simulations were performed using a time step of 0.25 fs for a total time of 500 ns.

Chemical Vapor Deposition of Graphene on Cu Foil. Monolayer graphene films with heavy grains were grown via LPCVD process on Cu foils (25 μm, 99.98% purity) of 1 x 1 cm$^2$ area using CH$_4$ (99.95% purity; Praxair) as carbon feedstock and H$_2$.
were washed with copious amount of acetone and IPA (in the sequential order). The native oxide of Cu foil was then removed by submerging in solution of Fe(NO3)2:HNO3 (1M:3M) for 10 min. Subsequently, the Cu foil was sonicated continuously with copious amount of water, acetone, and IPA (in the sequential order). In order to further remove the remaining surface ions, the Cu foil was sonicated in 100 mL of acetone (ACS spectrophotometric grade, ≥ 99.5%, Fisher Scientific). Then the foil was thoroughly washed with copious amount water, acetone, and IPA (in the sequential order), and then dried by purified air flow for 2 min. Further, the clean foil was loaded into the CVD furnace, and the reaction chamber was evacuated to 1 mTorr in 5 min. Next, 100 sccm of H2 was introduced in order to flush the system for another 10 min. The furnace temperature was increased to 1050 °C in 15 min, while maintaining the H2 gas flow. At 1050 °C, the Cu foil was annealed for 30 min to increase the grain size and to smoothen its surface. Then 10 sccm of CH4 was introduced into the chamber for 1 min ($P_{CH4} = 500$ mTorr). After the growth, the CH4 was turned off, and the chamber was quickly cooled down to room temperature by opening the half furnace.

**Graphene Transfer to h-BN/Si$_3$N$_4$/Si and Si$_3$N$_4$/Si Substrates.**

The graphene transfer from Cu foil to the desired substrates were performed as follows: First, 25 mg/mL of poly(methyl methacrylate) (PMMA) (MW 996,000, Sigma-Aldrich) in anisole (99% purity, Acros Organics) was spin-coated onto the graphene/Cu foil at (i) prespin of 4000 rpm for 30 s (1000 rpm/sec ramp rate) and (ii) full-spin of 4000 rpm for 30 s (1000 rpm/sec ramp rate). The PMMA-coated graphene/Cu foil was then air-dried for 5 min, followed by etching of the Cu foil with 1:3 of HNO3 (65% purity) and DI water for 1 h. The floating PMMA/graphene sample was picked up by submerging a clean quartz substrate into the solution and lifting up at 40° angle to the surface of etchant solution. Immediately, it was transferred onto DI water at the same manner as previous picking up step (repeated twice). The floating PMMA/graphene/graphene/Cu foil was picked up by the substrates (Si$_3$N$_4$/Si and directly grown h-BN on Si$_3$N$_4$/Si) with 40° angle to the surface of the DI water. These PMMA/graphene/Si$_3$N$_4$/Si and PMMA/graphene/h-BN/Si$_3$N$_4$/Si samples were left to dry overnight in the air. In order to remove the top PMMA layer, these samples were submerged into acetone for 10 min at room temperature, followed by washing with copious amount of acetone and IPA (in the sequential order) and dried with purified air flow for 2 min.

**Field Effect Transistor Device Fabrications.**

After transferring the graphene onto h-BN/Si$_3$N$_4$/Si and Si$_3$N$_4$/Si substrates, the samples were deposited with Cr/Au (15 nm/95 nm) layers. A positive photoresist (AZ 1818) was spin-coated onto the samples at 4000 rpm for 45 s. The samples were then baked on the hot plate at 110 °C for 1 min. Subsequently, a dose of UV light (365 nm and lamp power of 900 W) was introduced into the samples with aligned mask for 12 s using Karl Suss MA6 mask aligner. Then the samples were developed in a solution of 3:1 (DI water:AZ 340) for 18 s followed by etching the unprotected Cr/Au area to form the electrode contacts in Au etchant (36 s) and Cr etchant (18 s) at room temperature in the sequential order. After defining the metal contacts, the samples were washed with copious amount of acetone, IPA (in the sequential order), and dried with purified air flow for 2 min. The bar structure with a channel length of 27 μm and channel width of 7.5 μm (as shown in the manuscript Figure 4a) was fabricated by repeating previous steps with another layer of positive photoresist. After developing to form a protected pattern of graphene bar, these samples were placed inside Oxford reactive ion etching chamber to remove the nonprotected graphene via oxygen (O$_2$) plasma (10 W power, 20 s exposure, 535–550 V peak to peak voltage, and 260 V bias voltage). Subsequently, the covered photoresists were removed by submerging the samples into the first bath of AZ 1165 solution for 5 min, into the second bath of AZ 1165 solution for another 3 min to further remove the photoresists residues, and finally into IPA solution for 5 min. Finally, the samples were washed with copious amount of acetone and IPA (in the sequential order), and dried with purified air flow for 2 min.

**Device Pretreatment and Electrical Measurements.** Prior to electrical transport measurements, the samples were placed inside a clean 1” quartz tube in a split furnace. The chamber was evacuated to 1 mTorr in 5 min. Further, 20 sccm of H2 was introduced to flush the system for another 10 min. The furnace temperature was increased to 150 °C in 15 min, while maintaining the flow of H2 at 200 mTorr. At 150 °C, the photoresist residues were further removed by reducing gas (H2) for 2 h. After cooling down to room temperature, the samples were immediately placed inside the ARS cryostat system for electrical transport measurements.

**ASSOCIATED CONTENT**

© Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b01666.

Transverse optical (TO) phonon mode for silicon, lattice constant of directly grown h-BN films, AFM 3D topography images for Si$_3$N$_4$/Si and h-BN/Si$_3$N$_4$/Si surfaces, growth model for the synthesis of h-BN on silicon-based substrates, H-BN growth rate on Si$_3$N$_4$/Si and SiO$_2$/Si substrates, molecular dynamics simulation details, oxygen plasma treatment of silicon surfaces and characterizations, synthesis of h-BN on silicon surfaces with and without oxygen plasma treatment, lattice defects and point defects in graphene/h-BN and graphene/Si$_3$N$_4$ heterostructures, carrier concentration calculations, charge inhomogeneity point and electron–phonon scattering, temperature dependence of sheet resistivity, and charge carrier mobility in graphene/h-BN and graphene/Si$_3$N$_4$ at room temperature (PDF)

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**Author Contributions**

V.B. designed and supervised the work, discussed the results, and wrote the manuscript. S.B. designed and performed the experiments, discussed the results, and wrote the manuscript. P.N. performed the electrical transport measurements and analyzed the data. R.D. conducted AFM experiments, MD simulations, and analyzed the data. S.C. performed the XPS results and analyzed the data. S.B., P.N., R.D., S.C., M.R.S, and V.B. contributed to the scientific discussion and manuscript revisions.

**Notes**

The authors declare the following competing financial interest(s): M.R.S., V.B., and P.N. have submitted a patent application that covers direct growth of hexagonal boron nitride on silicon-based substrates and its heterostructure with graphene related to the content of this paper. R.D. and S.C. declare that they have no competing interests.

**ACKNOWLEDGMENTS**

V.B. acknowledges financial support from SunEdison Semiconductor, USA. This work made use of instruments in the Electron Microscopy Service (Research Resources Center, UIC) and Nanotechnology Core Facility of University of Illinois at Chicago. We acknowledge Dr. Daniel P. Bailey for detailed copy editing and discussion of the manuscript. V.B.
S.B. acknowledge Prof. Vivek Sharma and Dr. Fengguan Shi for valuable discussions.

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